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THE CHEMISTRY OF SYNTHETIC DYES

VOLUME II

CENTRAL FOOD TECHNOLOGICAL RESEARCH INSTITUTE, * MYSORE. *
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ORGANIC AND BIOLOGICAL CHEMISTRY
—A Series of Monographs—
EDITED BY LOUIS F. FIESER AND MARY FIESER

The Chemistry of
SYNTHETIC DYES

By

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University of Bombay

VOLUME II

CENTRAL FOOD TECHNOLOGICAL RESEARCH INSTITUTE, * MYSO
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1952
ACADEMIC PRESS INC., PUBLISHERS, NEW YORK

2533 ✓

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Library of Congress Catalog Card No. (52-5201)

~~F8,58~~ E1,87L

N52.2

PRINTED I AMERICA

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List of Abbreviations

Manufacturing companies:

AAP	American Aniline Products Inc., New York
AC	American Cyanamid Co. (Calco Chemical Division), Bound Brook, New Jersey
AGFA	Aktien-Gesellschaft für Anilin-Fabrikation, Berlin
BASF	Badische Anilin- und Soda-Fabrik, Ludwigshafen
BDC	British Dyestuffs Corporation, Huddersfield and Manchester
By	Farbenfabriken vorm. Friedrich Bayer and Co., Leverkusen
C	Leopold Cassella and Co., Frankfurt
CAC	Clayton Aniline Co., Manchester
Ciba (Cb)	Gesellschaft für Chemische Industrie in Basel
DH	Durand and Huguenin A.-G., Basel
DuP	E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware
GAFC	General Aniline and Film Corporation, New York
GDC	General Dyestuff Corporation, New York
GrE	Chemische Fabrik Griesheim-Elektron, Frankfurt
Gy	J. R. Geigy A.-G., Basel
ICI	Imperial Chemical Industries Ltd., Dyestuffs Group, Grangemouth, Huddersfield and Manchester
IG	Interessen Gemeinschaft für Farbenindustrie A.-G., Frankfurt
K	Kalle and Co., A.-G., Biebrich
Ku	Compagnie Nationale de Matières Colorantes et Manufactures de Produits Chimiques du Nord reunies Etablissements Kuhlmann, Paris
L	Farbwerk Mühlheim vorm. A. Leonhardt and Co., Mühlheim, Frankfurt
LBH	L. B. Holliday and Co. Ltd., Huddersfield
Lev.	Levinstein Ltd., Manchester
MLB	Farbwerke vorm. Meister, Lucius and Brüning, Hoechst
NAC	National Aniline Division, Allied Chemical and Dye Corporation, New York
PhC	Pharma-Chemical Corporation, Bayonne, New Jersey
S	Chemische Fabrik vorm. Sandoz and Co., Basel
SD	Scottish Dyes Ltd., Grangemouth
StD	Société Anonyme des Matières Colorantes et Produits Chimiques de St. Denis, Seine

Journals, Reports and Books:

Except for *JACS* (Journal of the American Chemical Society) and *JCS* (Journal of the Chemical Society, London), the abbreviations of *Chemical Abstracts* for the names of Journals have been followed. The indicated abbreviations have been used for the following.

Annual Repts. Chem. Soc. London	Annual Reports on the Progress of Chemistry, Chemical Society, London
Annual Repts. Soc. Chem. Ind. London	Reports on the Progress of Applied Chemistry, Society of Chemical Industry, London
BIOS	British Intelligence Objectives Sub-Committee Final Report No.
CI	Rowe, Colour Index, Society of Dyers and Colourists, Bradford, 1924
CIS	*Ibid.* Supplement
CIOS	Combined Intelligence Objectives Sub-Committee Report
FIAT	Field Intelligence Agency Technical Report
OSCV	*Organic Syntheses Collective Volume;* I, 2nd ed., 1941; II, 1st ed., 1943
ST	Schultz, *Farbstofftabellen*, 7th ed., Akademische Verlagsgesellschaft, Leipzig, 1931
ST II	*Ibid.* Zweiter Band, 1932
ST Erg. I	*Ibid.* Ergänzungsband I, 1934
ST Erg. II	*Ibid.* Ergänzungsband II, 1939

Patents:

BeP	Belgian Patent
BP	British Patent
CP	Canadian Patent
DP	Dutch Patent
DRP	German Patent
FP	French Patent
IP	Indian Patent
JP	Japanese Patent
NP	Norwegian Patent

RP	Russian Patent
SP	Swiss Patent
SwP	Swedish Patent
USP	United States Patent

Substituent groups:

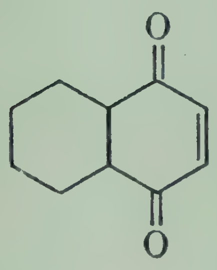
Ac (acetyl); AQ (anthraquinonyl, α or β); Ar (aryl); Et (ethyl); Me (methyl); Ph (phenyl); R (alkyl or aralkyl).

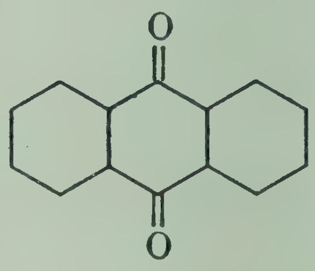
Notes on the Text

Temperatures are in degrees Centigrade.

Double bonds are not shown in benzene, naphthalene, anthracene, pyridine, and other aromatic ring systems. In α-naphthoquinone (I) and anthraquinone (II) the double bonds in the benzene rings are omitted. It is more convenient to represent the phenazthionium cation as (III), instead of (IV). Unless otherwise indicated, rings have been numbered as in Patterson's Ring Index, Reinhold, New York, 1940.

(I)





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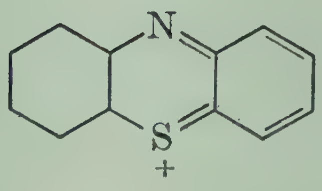
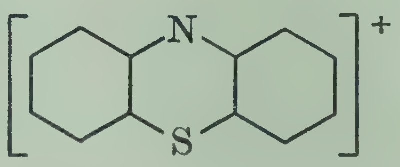
(III)





(IV)

The methyl group is numbered 1 for all toluene derivatives including the cresols and the toluidines; xylene derivatives are stated as derivatives of *o*-, *m*- and *p*-xylene; thus 5-chloro-*o*-toluidine is 5-chloro-2-aminotoluene, and *m*-4-xylenol is 2,4-dimethylphenol. Other substituents are numbered in the following order of precedence: carboxyl, hydroxyl, alkoxyl, amino and sulfonic groups. Thus the numbering of salicylic and anthranilic acid derivatives starts from the carboxy group, and of anisidine derivatives from the methoxy group.

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Errata for Volume I—see p. xii

Errata in Volume I

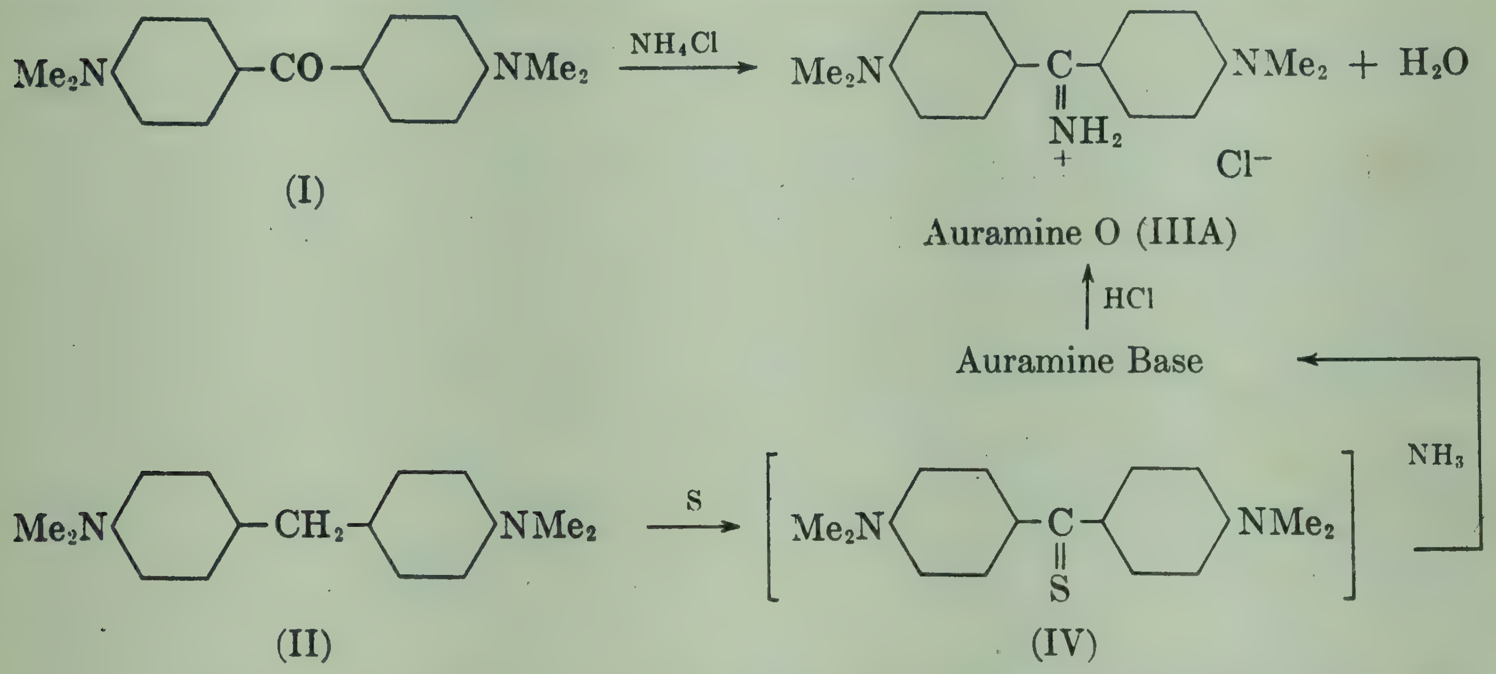
p. 6, line 26, replace "4–8" by "4,8"
p. 71, ref. 86, replace "Mason" by "Masson"
p. 95, line 7, replace "or" by "of"
p. 112, last line, replace "acetic" by "*n*-caproic"
p. 127, ref. 288, replace "645" by "639"
p. 155, ref. 404, replace "140" by "1407"
p. 189, ref. 494, replace "Battegey" by "Battegay"
p. 309, legend to Fig. 2, delete "(Wright)"
p. 312, legend to Fig. 3, delete "(Wright)"
p. 320, line 12, replace "100 × 0 × 12" by "100 × 10 × 12"
p. 329, legend to Fig. 1, read as
" . . . Absorption of phenol in alcohol (- - - - -) . . . "
p. 348, ref. 45, replace "Hamer" by "Hamner"
p. 367, ref. 75, replace "Katzellenbogen" by "Katzenellenbogen"
p. 369, ref. 77, replace "Katzellenbogen" by "Katzenellenbogen"
p. 371, ref. 82, replace "(1948)" at the end by "(1949)"
p. 373, legend to Fig. 18, line 2, read as
"- - - - -, after refluxing in the dark for 45 minutes;"
p. 374, legend to Fig. 19, line 2, read as
"- - - - -, on iodine catalysis."
p. 504, line 5, replace "s" by "is"
p. 577, line 16, insert ")" before ";"
pp. 702–703: According to BIOS 1661, the diazo component for Vulcan Fast Yellow 5G is 2,2′-dichloro-5,5′-dimethoxybenzidine; for Permanent Red F2R it is 2,5-dichloroaniline; and for Vulcan Fast Red GF it is dianisidine.
Group together Lithol Fast Orange RN and Permanent Red GG; Lithol Fast Scarlet GRN and Helio Red RBL; Helio Fast Red RBR and Sudan II.
Delete the line in which Permanent Red FFR occurs for the second time.

CHAPTER XXIII

DIPHENYLMETHANES AND TRIPHENYLMETHANES

DIPHENYLMETHANES

Almost the only commercial representative of the diphenylmethane class is Auramine O (CI 655); but this dye, discovered in 1883 (Kern; Caro) is still one of the most widely used synthetic dyes, the annual production being several million pounds. The original method of preparation, which was employed technically by BASF, was to heat 4,4′-bis-dimethylaminobenzophenone (Michler's ketone; I) with ammonium chloride and zinc chloride at 150–160°. The method now used was developed by Sandmeyer (1889); 4,4′-bis-dimethylaminodiphenylmethane (II), sulfur, ammonium chloride and a large amount of common salt as diluent are heated to about 200° in a current of ammonia.[1] The product is Auramine Base, which is dissolved in hydrochloric acid, and the dye is then salted out. The thioketone (IV) can be first prepared (80% yield) by the thionation of (II), and used for subsequent conversion into Auramine or triphenylmethane dyes via the ketone dichloride.[2] Auramine O is a yellow basic dye, which has poor fastness; being a ketonimine, it is readily hydrolyzed by hot acids and alkalis, with the elimination of ammonia and the formation of Michler's ketone. In spite of these defects the dye is extensively used for dyeing and printing tannin-mordanted



(I)

Auramine O (IIIA)

Auramine Base

(II)

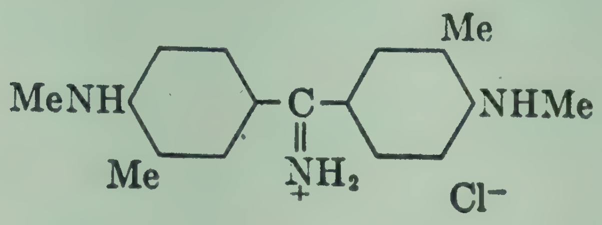
(IV)

---

[1] Lynch and Reid, *JACS* **55**, 2515 (1933).

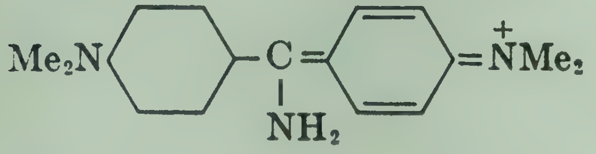
[2] *BIOS* **959**.

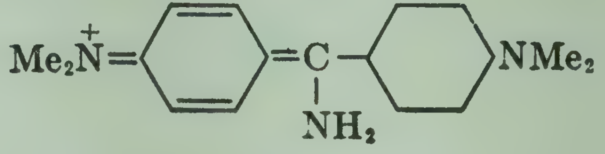
cotton, dyeing paper, silk, leather and jute, and for the manufacture of lakes, because of its cheapness and the brilliance of the pure yellow shades. One of the chief uses is for dyeing wool, the shade being fast to stoving. The greenish Auramine G (Gnehm and Schmid, 1892) (BASF; CI 656) is also made by the Sandmeyer process, using the


Auramine G

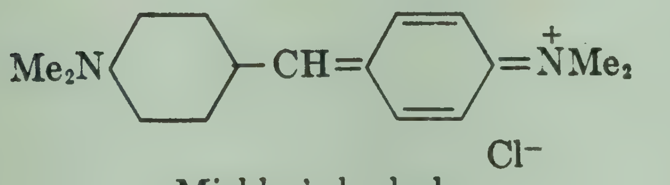
diphenylmethane derivative obtained by the condensation of mono-methyl-*o*-toluidine with formaldehyde.

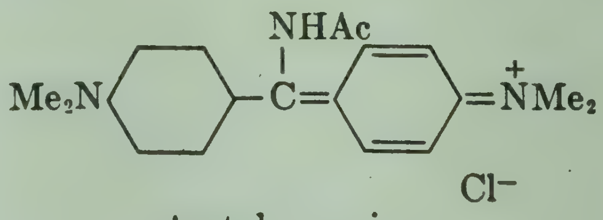
The cation of Auramine O is a resonance hybrid of the structures (III A, B and C). The fact that the dye is only yellow in color (λmax.


(IIIB)


(IIIC)

4200A) is explicable when it is considered that the positive charge associated with the electronic transition along an approximately horizontal path (B ↔ C) is diminished as a result of the contribution made by the structure (A) to the resonance. In the cation of the hydrochloride of Michler's hydrol, the full positive charge is available for the horizontally polarized transition, and the colorless Michler's hydrol forms intensely blue salts (λmax. 6200A). For a similar reason, the *N*-acetyl derivative of Auramine Base is yellow in color, while the salts are deep violet to


Michler's hydrol
hydrochloride


Acetylauramine
hydrochloride

bluish green; acetylation greatly reduces the ability of the nitrogen attached to the methane carbon atom to acquire a positive charge, so that a correspondingly larger charge is available for the transition polarized along the length of the molecule. The experimental observations of Semper[3] and others, which were regarded as supporting the original Graebe formula (IIIA) for Auramine, are in complete agreement with its constitution as a resonating molecule.

Diphenylmethane (m.p. 24–25°) is obtained by the condensation of benzene with benzyl chloride in presence of aluminum chloride (Friedel and Balsohn, 1880) or aluminum amalgam[4] or various other agents.

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[3] Semper, *Ann.* **381,** 234 (1911).

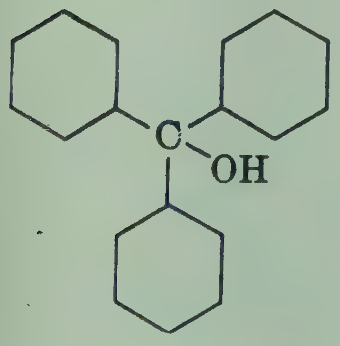
TRIPHENYLMETHANES

Magenta and other triphenylmethane dyes were among the earliest synthetic coloring matters, and they still remain an important and numerous group. The formation of Magenta was independently noticed by Natanson in 1856 and by Hofmann in 1858; Verguin in 1859 achieved the first technical preparation of Magenta by heating crude aniline with stannic chloride. Various other oxidizing agents were subsequently used, and nitrobenzene (Coupier, 1868) has survived. During the next few years, new methods for making triphenylmethane dyes, which have displaced the old Magenta process except for Magenta itself, were developed: the phosgene process for Crystal Violet (Kern, 1883), condensations with the chloride of Michler's ketone (Caro, 1883), and oxidation of diphenylmethane bases in the presence of aniline derivatives (Weinberg, 1889).

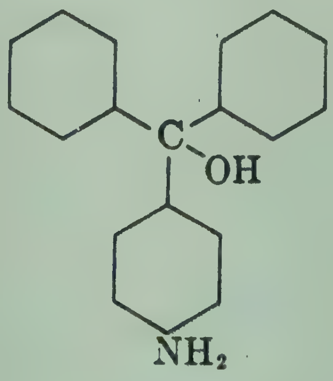
CONSTITUTION OF THE TRIPHENYLMETHANE DYES

Because of the empirical character of the Magenta process and the complex series of reactions which were involved, it took some twenty years for the complete elucidation of the structure of Magenta and its derivatives. Hofmann showed in 1862 that Magenta is the salt of a base which he named Rosaniline, and which yields on reduction a second base, leucorosaniline, characterized by its forming colorless salts with acids in contrast to the deep color of Magenta. Hofmann was followed by several other investigators, and finally O. and E. Fischer succeeded in determining the constitution of Magenta.[5]

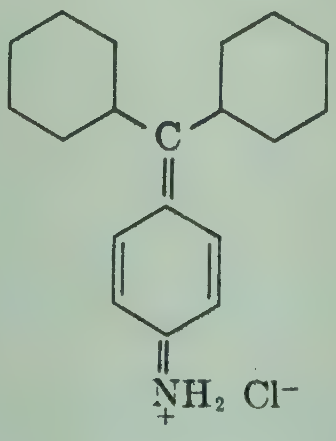
All the dyes of the series are derived from the hydrocarbon, triphenylmethane, and the tertiary alcohol, triphenylcarbinol, which are both colorless. One or more primary, secondary or tertiary amino groups or hydroxyl groups para to the methane carbon atom are necessary for converting the carbinol into a dye. When the colorless *p*-aminotriphenyl-



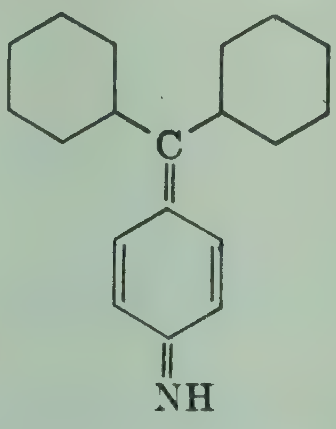
Triphenylcarbinol
m.p. 162°



(I)



(II)



Fuchsone-imine

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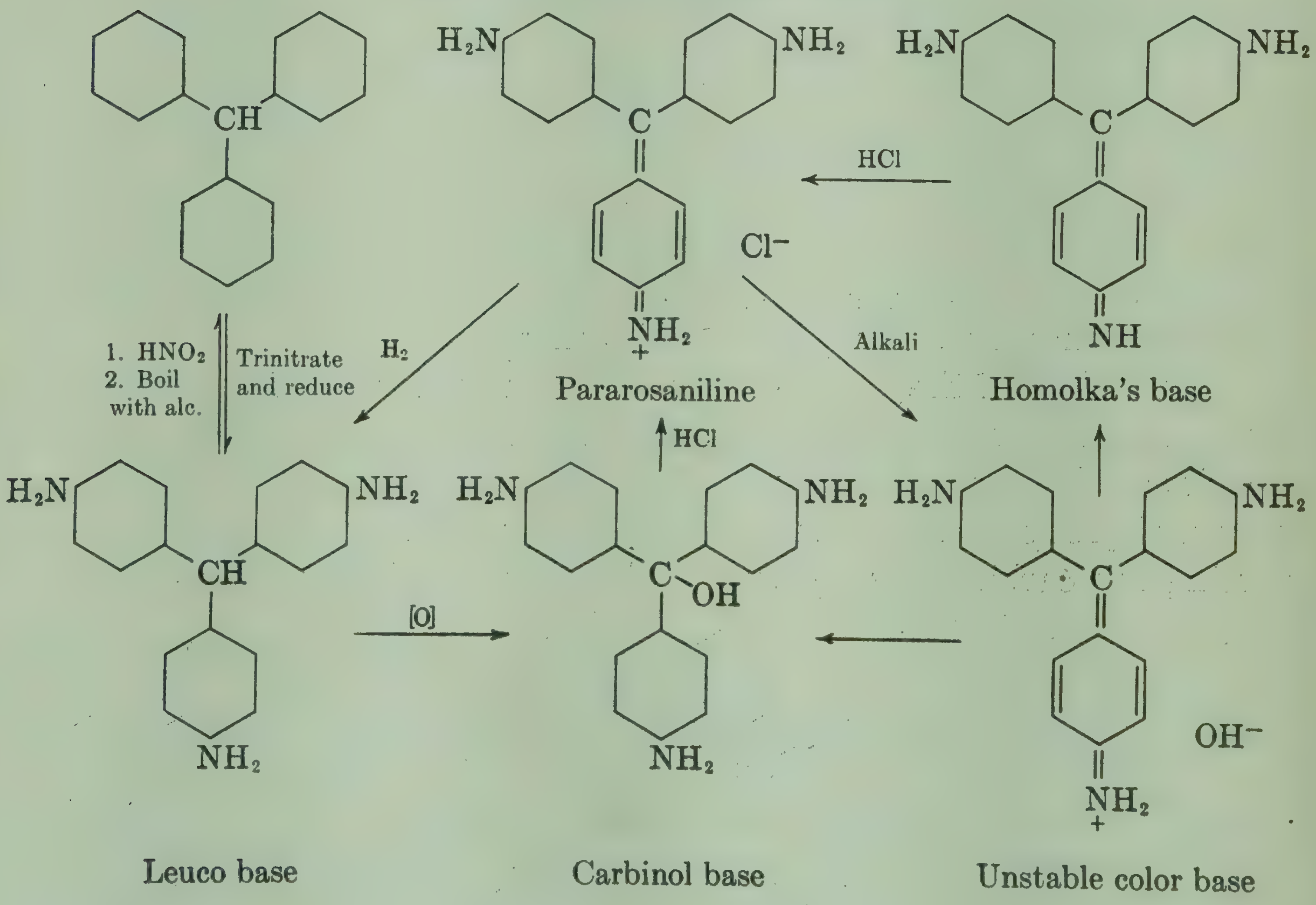
[4] Hirst and Cohen (1895); Hartman and Phillips, *OSCV* II, p. 232.

[5] *Ber.* **13**, 2204 (1880).

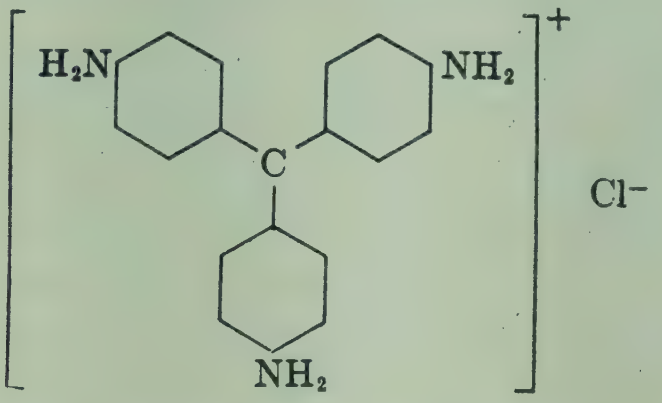
carbinol (I) is treated with hydrochloric acid, salt formation takes place with the elimination of a molecule of water, and an orange-red dye (II) is formed. The introduction of a *p*-amino group in a second benzene ring in (II) gives Doebner's Violet, which like (II) is of no practical value; and the introduction of *p*-amino groups in both the unsubstituted rings of (II) gives Pararosaniline. Baeyer and Villiger prepared fuchsone-imine, the anhydride of (I), in the dimeric form. Homolka was successful in preparing from Pararosaniline (fuchsine), by the action of alkali, the brownish-yellow "Homolka's base" in the monomolecular form. Homolka's compound dissolves in hydrochloric acid, forming a deep red ammonium salt, Pararosaniline. On reduction, the dye is converted into a colorless leuco compound, oxidation of which (e.g., by means of lead peroxide) gives the carbinol base; this is also formed by isomerization of the unstable color base, which is first obtained when Pararosaniline is treated with potassium hydroxide. The carbinol base combines readily with acids to give Pararosaniline.

CHART 1
REACTIONS OF PARAROSANILINE


CH
H₂N
NH₂
C
Cl⁻
NH₂
+
Pararosaniline
HCl
Homolka's base
NH
1. HNO₂
2. Boil with alc.
Trinitrate and reduce
H₂
Alkali
HCl
CH
C
OH
[O]
OH⁻
Leuco base
Carbinol base
Unstable color base

Triphenylmethane (m.p. 92°) can be synthesized by the condensation of benzene with carbon tetrachloride to form the aluminum chloride complex of triphenylmethyl chloride (trityl chloride; Ph_3CCl), which is then reduced to the hydrocarbon by means of ether.[6] Pararosaniline and triphenylmethane can be interconverted as shown in Chart 1. The position of the amino groups in Pararosaniline and its homologs has been proved in an unambiguous manner. Benzaldehyde condenses with two moles of aniline in presence of zinc chloride or sulfuric acid to form diaminotriphenylmethane; tetrazotization and hydrolysis give the corresponding dihydroxy compound. Fusion of this dihydric phenol with potassium hydroxide gives the known 4,4′-dihydroxybenzophenone, so that the *p*-orientation of the two amino groups in diaminotriphenylmethane is clear. The condensation of *p*-aminobenzaldehyde with two moles of aniline yields leuco Pararosaniline, and by analogy with the benzaldehyde condensation, all the three amino groups in leuco Pararosaniline, and therefore in the carbinol base and in Pararosaniline, are *para* to the methane carbon atom.

Pararosaniline and other triphenylmethane dyes are resonance hybrids, in which the major contributing structures carry the cationic charge on one of the nitrogen atoms or the methane carbon atom. They are therefore best represented as (III), but it is more convenient to write structures (cf. Chart 1) in which the positive charge is assigned to one of the nitrogen atoms.[7, 8]



(III)

Classification and Properties

The triphenylmethane dyes may be divided into three groups: (1) Malachite Green series, which contain two amino groups; (2) Rosaniline series which contain three amino groups; and (3) Rosolic acid series which contain three hydroxyl groups.[2, 9–13] In all the three series, the amino or hydroxyl groups are in different benzene rings and are *para* to the methane carbon atom. The typical shades of the triphenylmethane dyes are red, violet, blue and green, which are notable for their intensity and brilliance. From the point of view of application, the triphenylmethane dyes belong to four classes: (a) basic dyes, applicable to cotton on a tannin-mordant, and to wool and silk from a faintly acid bath; (b) acid colors for wool and silk; (c) mordant dyes which may be applied as chrome colors for wool, and as chrome-printing colors for cotton; and (d) lakes of the basic and acid dyes, e.g., with phosphomolybdotungstic acid. The basic dyes are usually marketed as zinc chloride double salts, hydrochlorides or oxalates. The zinc-free dyes are necessary for use as bacteriological and histological stains, and are advantageously used for certain dyeing and printing processes. The solubility of some basic dyes is improved by converting them into hydrofluorides,[14] sulfamates,[15] phosphates,[16] or glycerophosphates.[14] Most basic dyes of the triphenylmethane series are beautiful, crystalline compounds with a reflex, the color of which is often complementary to the color in solution. The aqueous solutions undergo color changes with acids;[7] with alkali they form colorless carbinols, and with reducing agents the colorless leuco compounds. Like other basic dyes, the triphenylmethanes have poor fastness to light and alkali; but because of their cheapness, high tinctorial power and the brilliance of the shades, they are still largely used and are specially valued in calico printing. In wool dyeing they are less useful, since acid colors are available which are faster than the basic dyes and otherwise comparable with them.

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[6] Norris, *OSCV* I, p. 548. Trityl chloride is useful for the characterization of alcohols as the trityl ethers.

[7] See Chapter VIII.

[8] For a discussion of the structure and absorption of the triphenylmethane dyes, see Ramart-Lucas, *Bull. soc. chim.* **12**, 477 (1945).

[9–12] The preparation of a large number of triphenylmethane dyes has been described in (2); (9) *BIOS* **961**; (10) *BIOS* **1433**; (11) U.S. Dept. of Commerce Textile Series **19**; (12) Microfilm PB 19,933.

[13] Plant employed for the manufacture of triphenylmethane and other basic dyes is described in *BIOS* **1157**.

The mechanism of fading of triphenylmethane dyes has been examined by Iwamoto;[17] in the presence of sunlight and air, Malachite Green and Crystal Violet are converted into *p*-dimethylaminobenzophenone and Michler's ketone respectively. Exposure of the dyes to sunlight in the absence of air merely yields the corresponding leuco compounds, and in the fading of these dyes oxidation plays an important role.

The acid colors of the triphenylmethane series include several important blue and green dyes. The blue and violet chrome-mordant dyes are valuable in wool dyeing and in calico printing. In recent years acid and acid-mordant triphenylmethane dyes with improved light fastness have become available as a result of the discovery that specific groups and ring systems (e.g., β-alkoxyethyl groups, *p*-anisidino and *p*-toluidino groups, indolyl residues) have a favorable effect on light fastness. The introduction of a *p*-alkoxy- or *p*-alkyl-diphenylamine nucleus also appears to exercise a beneficial effect on the light fastness of triarylmethane dyes. It is, however, necessary to introduce a number of *N*-β-hydroxyethyl or β-alkoxyethyl groups in order to give the dye adequate solubility.[18] Dyes which dye wool and silk in clear blue shades of good fastness to light, but in addition have the property of being dischargeable to a pure white shade, are obtained when a replaceable atom or group (e.g., Cl, OMe, SO_3H or NO_2) *para* to the central carbon atom in an acid triarylmethane dye is made to react with an *o*- or *p*-phenylenediamine or *N*-monoacyl derivative.[19] *N*-Alkyl- or -aryl-*o*- or *p*-phenylenediamines also give dyes with similar properties.[20] The acid triarylmethane dyes obtained from *p*-chloro- or *p*-sulfobenzaldehyde can be condensed with *p*-aminophenyl β-hydroxy- or -ethoxyethyl ether to give dyes which possess very good fastness to light.[21] The resulting dyes contain the group $C_6H_4NHC_6H_4$—O—C_2H_4OH (or OEt). IG have been particularly active in this field, and other examples are quoted later.

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[14] Schaefer and General Aniline and Film, USP 2,425,569; 2,435,905.

[15] Wyler and ICI, BP 495,782.

[16] IG, BP 396,177.

[17] Iwamoto, *Bull. Chem. Soc. Japan* **10,** 420 (1935).

By precipitating basic triphenylmethane dyes with complex acids, such as phosphotungstic, phosphomolybdic, and especially phosphomolybdotungstic acid, bright pigments (e.g., Fanal colors, IG) with good light fastness have been produced. These complex acids, silicotungstic acid being preferred, can be used for estimation of basic dyes by precipitating them from solution and igniting the precipitates.[22] Cuprous ferrocyanides of basic dyes can be made fast by an ageing process, in which a stable molecular complex is formed.[23] Modified hydrous zirconia precipitates basic dyes, and the pigments are brilliant and soft in texture.[24]

Malachite Green Series

Malachite Green (CI 657) is made by heating together benzaldehyde (1 mole), dimethylaniline (2.5–2.75 moles) which must be free from monomethylaniline, and hydrochloric acid or sulfuric acid as condensing agent at 100° for 24 hours; the reaction vessel is provided with mechanical agitation and a reflux condenser.[25] The excess of dimethylaniline is to ensure that the whole of the more expensive benzaldehyde is utilized in the reaction. The reaction proceeds in two stages;[26] the benzhydrol is first formed, but it can be isolated only in small quantities, since it condenses very readily with a second mole of the amine. Excess of the acid condensing agent must be avoided, although this is not for the reason, considered originally, that excess acid led to the formation of the benzhydrol which was incapable of reacting further to form the triphenylmethane. About two-third mole of acid gives the optimum results. At the end of the reaction, the mixture is made alkaline with caustic soda, and distilled to remove excess of dimethylaniline. The residual leuco base is dissolved in ice-cold hydrochloric and acetic acids, and oxidized with the theoretical quantity of freshly prepared lead peroxide. Lead is then precipitated with sodium sulfate, the clear filtrate boiled, and treated with ammonia to precipitate the carbinol. Malachite Green is finally isolated as the zinc chloride doublt salt, or as the oxalate (Diamond Green). Malachite Green as the oxalate is crystallized in wooden vats in which copper rods are suspended. Malachite Green is a largely used dye, although the bluish green shade on tannin-mordanted cotton has poor light fastness and is very sensitive to alkali. The zinc-free compound is used as a bacteriological and histological stain. In medicine it has some use as an external antiseptic for wounds and ulcers, and subcutaneous injections of the solution in normal saline have been used in the treatment of trypanosomiasis. The ionization of basic triphenylmethane dyes has

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[18] IG, BP 425,041.

[19] IG, BP 439,200.

[20] IG, BP 449,090.

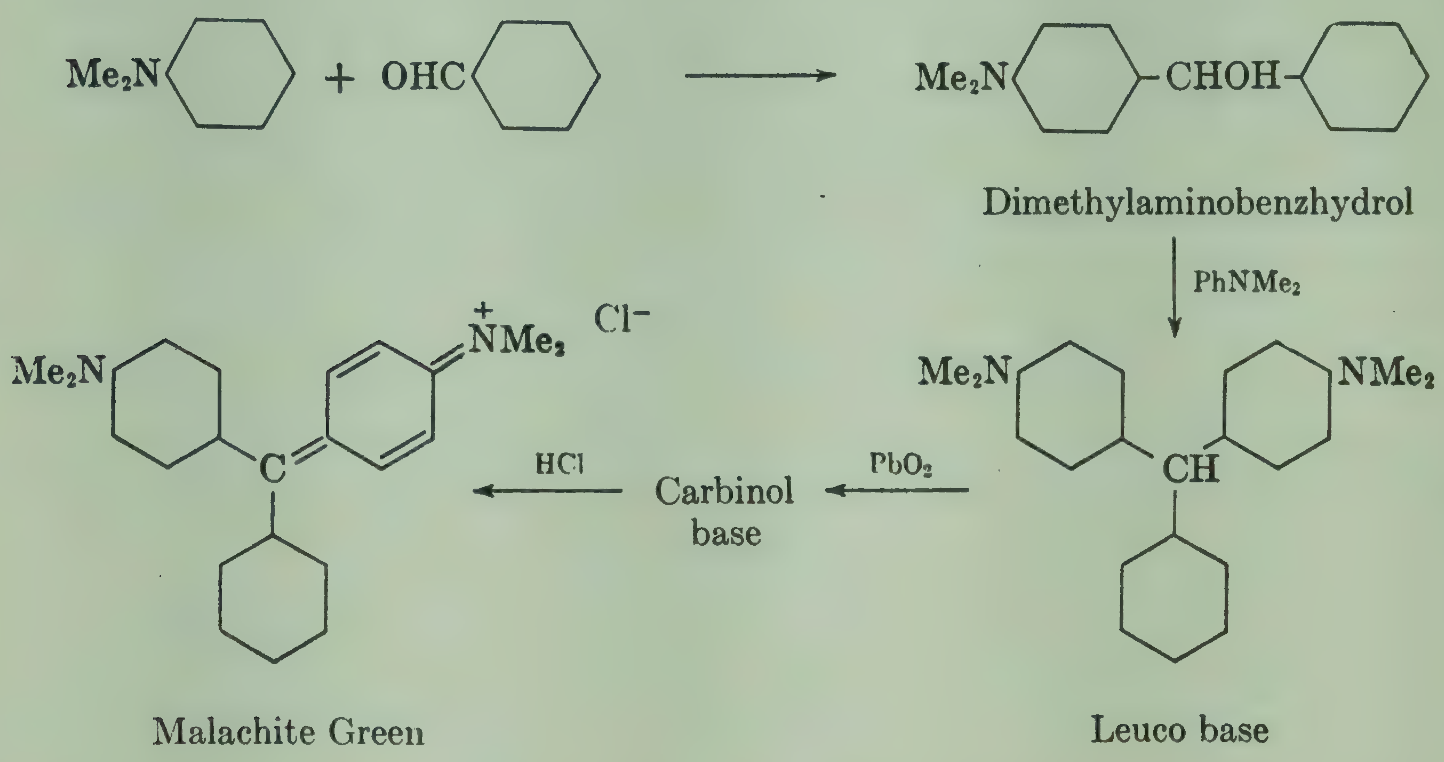
[21] Linch, Stocks and ICI, BP 443,104.

[22] Kozlov, *J. Applied Chem. U.S.S.R.* **9**, 558 (1936).

[23] Michels, BP 407,856.

[24] Blumenthal, *Am. Dyestuff Reptr.* **37**, 285 (1948); Wainer and Mater, USP 2,452,616.

[25] The addition of urea shortens the reaction time and increases the yield; Yoshino, *Repts. Tokyo Imp. Ind. Research Inst. Lab.* **37**, 95 (1942).



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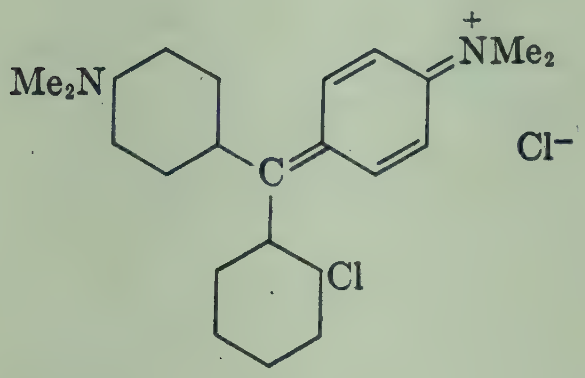
[26] Tomoika, *J. Soc. Chem. Ind., Japan* **34,** 176B (1931); Davies and Hodgson, *J. Soc. Dyers Colourists* **59,** 196 (1943).

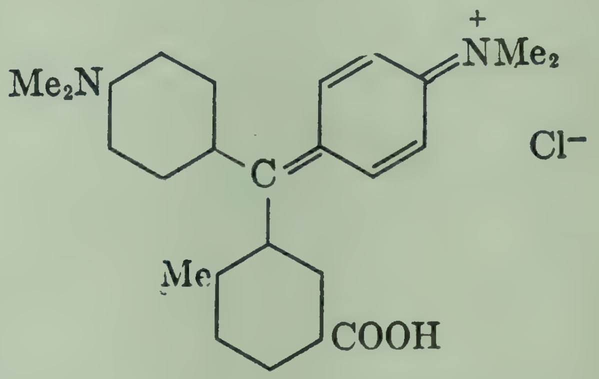
Michler's ketone reacts with chlorobenzene in boiling toluene in presence of sodium to yield Malachite Green; Rodd and Linch, BP 272,321; 301,193; *JCS* 2174, 2179 (**1927**).

been studied recently from the point of view of their biological action.[27]

The benzaldehyde synthesis of Malachite Green is a general reaction, applicable to other aromatic aldehydes and tertiary amines. The analog of Malachite Green prepared from diethylaniline is used as the sulfate, Brilliant Green or Fast Green (Bindschedler and Busch, 1879; CI 662), which is a powerful bactericide useful for external application; for dyeing, the oxalate or zinc chloride double salt may be used and is valued for the pure green shades it gives on wool and silk and in calico printing. When certain *o*-substituted benzaldehydes are used in the Malachite Green condensation, the dyes have improved fastness and the shades are bluer. The *o*-chlorobenzaldehyde derivative, Setoglaucine O (Sandmeyer and Schmid, 1896) (Gy; CI 658), is a faster and bluer shade of green than Malachite Green, and is useful for silk dyeing; Astrazone Blue G (IG) and Rhoduline Blue 6G (IG) possess the same constitution. Astrazone Blue B (Rhoduline Blue 5B; IG) is the analog from *N*-ethyl-*o*-toluidine.[28] The Astrazones are water-soluble dyes for cellulose acetate, which are specially useful for printing; the shades are bright and have good fastness to light. Brilliant Glacier Blue (Ciba) (CI 664) is made from monomethyl-*o*-toluidine and 2,5-dichlorobenzaldehyde. Turquoise Blue (By; CI 661), prepared from 2-nitro-5-methylbenzaldehyde and dimethylaniline, gives an alkali-fast, clear shade of blue, and is used in calico printing and the manufacture of lakes. Chrome Turquoise Blue B (By) is prepared by the condensation of Michler's hydrol with *p*-toluic acid in presence of sulfuric acid, and subsequent oxidation with lead peroxide and hydrochloric acid.[10]



Astrazone Blue G
Rhoduline Blue 6G



Chrome Turquoise Blue B

Acid dyes of the series are obtained by introducing sulfonic groups. Direct sulfonation of basic dyes containing only alkylamino groups is unsatisfactory, and the usual procedure is to employ dyes containing *N*-benzyl groups which are convenient carriers of sulfonic groups. In the

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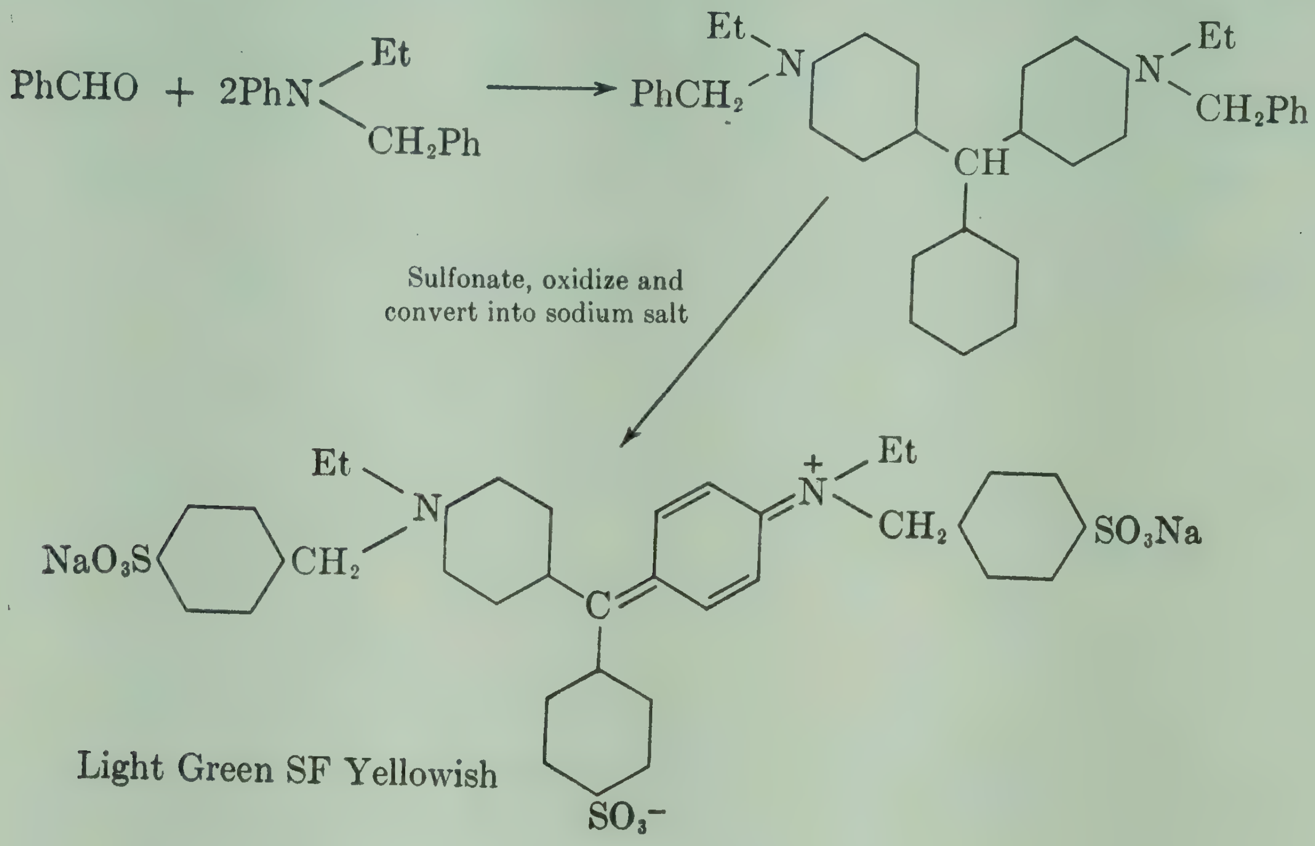
[27] Goldacre and Phillips, *JCS* 1724 (**1949**).

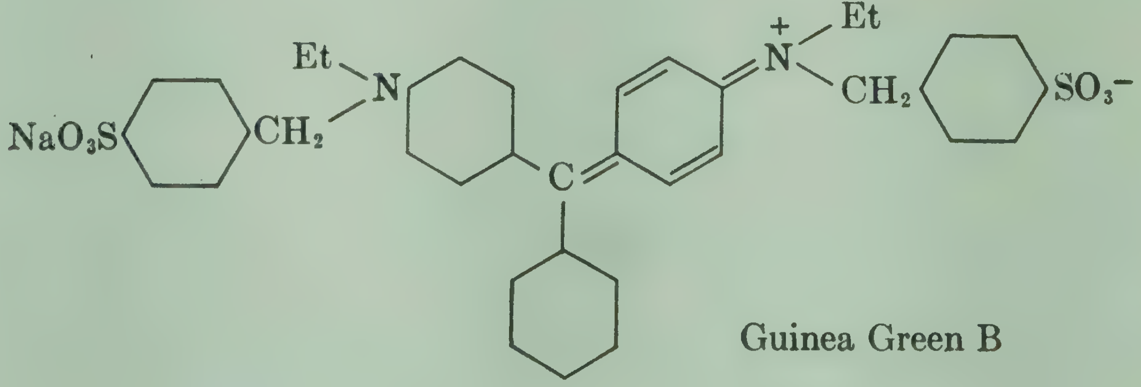
[28] *BIOS* Misc. Report 20.

Malachite Green series, the unsubstituted benzene ring is sulfonated simultaneously. Light Green SF yellowish (Koehler, 1879) (BASF; CI 670) is prepared by condensing benzaldehyde with benzylethylaniline, sulfonating the leuco base, oxidizing and converting into the sodium salt. The free trisulfonic acid is marketed as Acid Green Conc. F extra strong (IG).[10] Light Green SF contains a mobile sulfo group, and when this is displaced by the *p*-phenetidino group it gives a blue of good fastness to light. When it is heated with *o*- or *p*-phenylenediamine it gives blue dyes said to be useful for silk, being dischargeable to a pure white.[29] Brilliant Acid Blue B (By) is prepared by the disulfonation of the basic dye from *o*-chlorobenzaldehyde and benzyl-*o*-toluidine;[10] the corresponding trisulfonic acid has been stated to be Neptune Green SBX (IG), which is level dyeing, but has low light and milling fastness (2).[30]


PhCHO + 2PhN
Et
CH₂Ph
PhCH₂
N
Et
N
Et
CH₂Ph
CH
Sulfonate, oxidize and convert into sodium salt
Et
N
NaO₃S
CH₂
C
N
Et
CH₂
SO₃Na
SO₃⁻

Light Green SF Yellowish

Alternatively, we may employ for the condensation with benzaldehyde a benzylethylanilinesulfonic acid; Guinea Green B (Schultz and Streng, 1883) (AGFA; CI 666) is prepared in this manner.


Et
N
NaO₃S
CH₂
C
N
Et
CH₂
SO₃⁻

Guinea Green B

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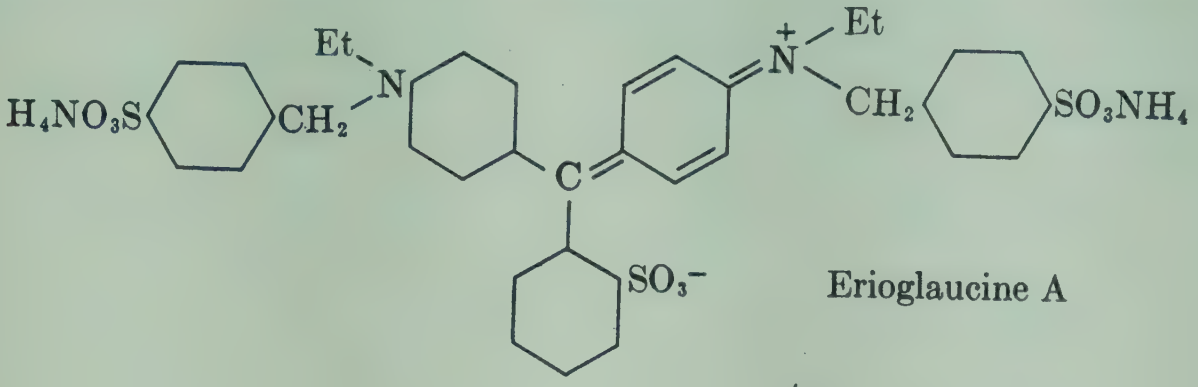
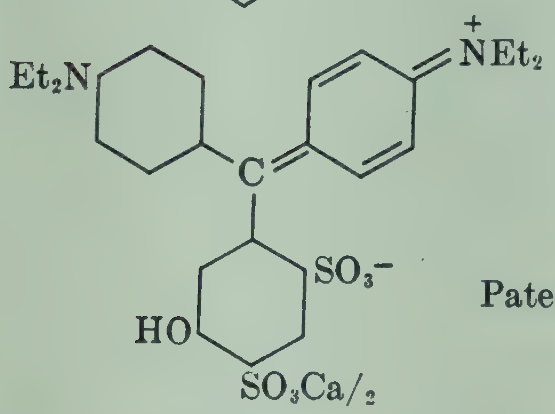
[29] IG, *GP. Anm. I.* 47,362.

[30] Microfilm FD 2537/46.

Patent Blue V (Hermann, 1888) (MLB; CI 712) is made by condensing *m*-hydroxybenzaldehyde with two moles of diethylaniline, sulfonating the leuco base, oxidizing and converting into the calcium salt. In the original method (MLB) *m*-nitrobenzaldehyde was used in the condensation, the nitro group in the leuco base being then replaced by hydroxyl, via the amine and diazonium salt. The importance of this series of dyes lies in their slightly increased fastness to light, and the much more marked improvement in fastness to alkali and level dyeing character. These properties were ascribed to the hydroxyl group *meta* to the methane carbon atom; but the significant factor was shown later to be the *o*-sulfonic group. By using benzaldehyde-*o*-sulfonic acid, or its derivatives, and other tertiary amines in place of diethylaniline, a series of dyes with good light fastness are obtained. Examples are the greenish blue Erioglaucine A (Sandmeyer, 1896) (Gy; CI 671) (Patent Blue AE, B; Neptune Blue BR, IG)[12] and Xylene Blue VS (S; CI 672). The IG dyes, Patent Blue AF, V New, Brilliant Indo Blue 5G, Cyanol FFG and Cyanol extra are prepared from benzaldehyde-2,4-disulfonic acid, which is condensed with benzylethylaniline, diethylaniline, dibenzylaniline, *n*-butyl-*o*-toluidine and monoethyl-*o*-toluidine respectively.[10] When bis-diethylaminobenzhydrol is condensed with *m*-xylene-4-sulfonic acid, the leuco compound sulfonated to a disulfonic acid and oxidized, the product is Guinea Fast Green B (IG).[11, 12] The condensing agent for these aldehyde-amine condensations is sulfuric acid as monohydrate, and the leuco compound is oxidized to the dye by means of sodium dichromate. Patent Blue VF and VF Special (IG) are made from V New, the first being the sodium salt appearing red in the crystalline state, and the second the free acid which appears green.[10]

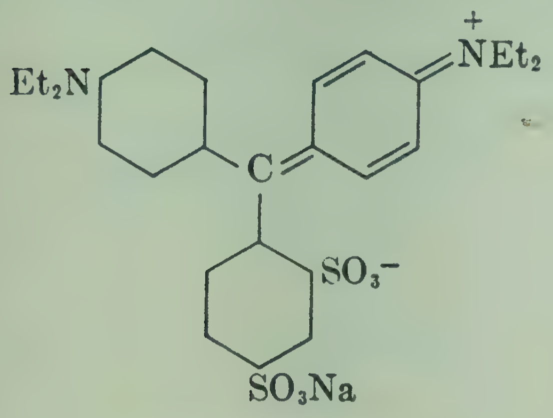


Erioglaucine A

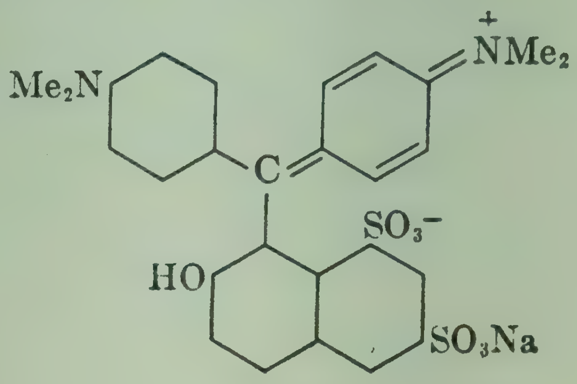


Patent Blue V

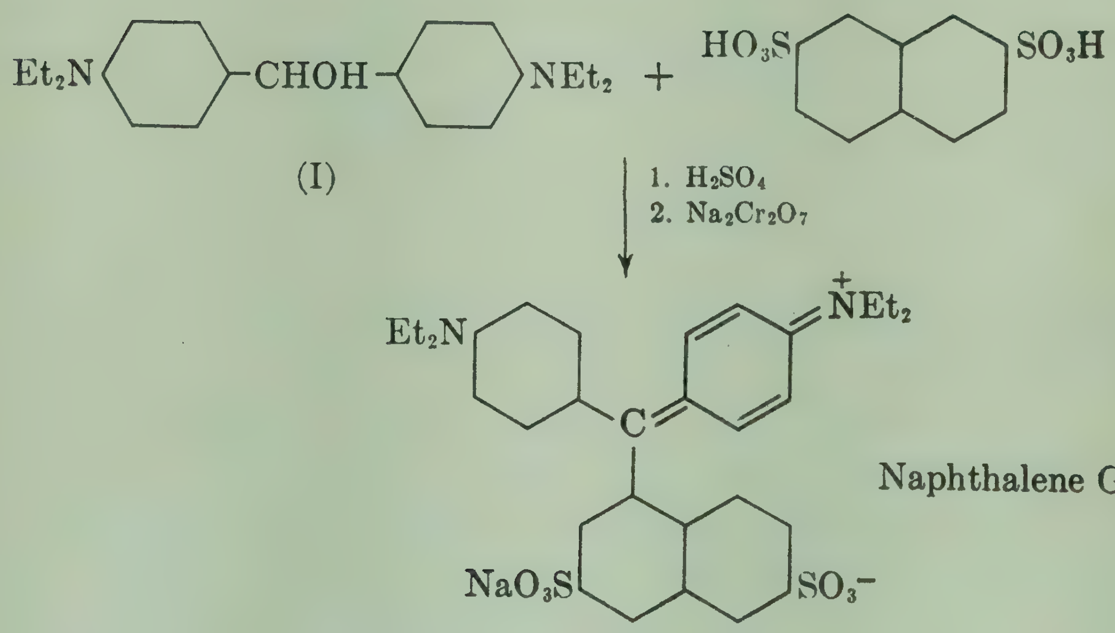
Useful green acid dyes of the Malachite Green series are obtained by replacing the benzene ring not carrying an alkylamino group by a naphthalene residue. Dyes of this type are prepared by condensing a bis-dialkylaminobenzhydrol (I) with a naphthalene- or naphthol-sulfonic acid. Examples are Naphthalene Green V (Hermann, 1899) (MLB; CI 735)[12, 31] and Wool Green S (BASF; CI 737) made by condensing the appropriate benzhydrol with naphthalene-2,7-disulfonic acid and β-naphthol-3,6- or 6,8-disulfonic acid respectively in presence of sulfuric acid, and then oxidizing with dichromate. For Wool Green S β-naphthol may be used, together with oleum as condensing agent, when sulfonation also takes place. The benzhydrol is prepared by oxidation of the tetraalkyldiaminodiphenylmethane with manganese dioxide and sulfuric acid, and it is used without isolation for the condensation with the naphthol or naphthalene sulfonic acid. Finely divided manganese dioxide for such oxidations is freshly prepared from manganese sulfate, a by-product from the manufacture of benzaldehyde disulfonic acid, and potassium permanganate in sodium carbonate solution.



Xylene Blue VS



Wool Green S



(I)

Naphthalene Green V

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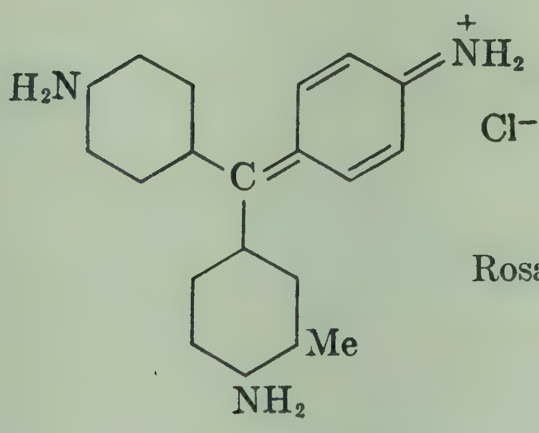
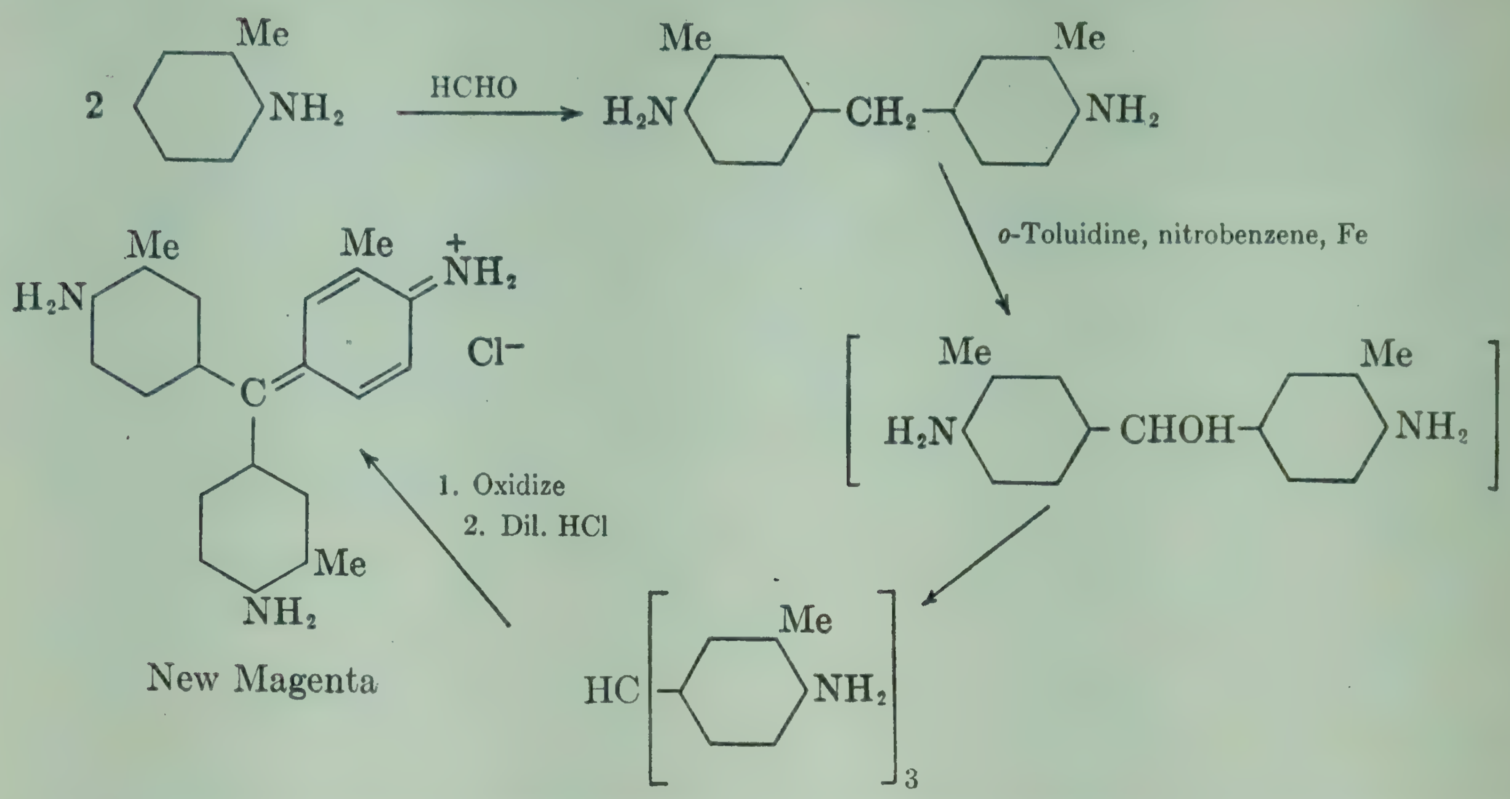
[31] See also British Dyestuffs, DRP 485,663.

MAGENTA SERIES

When Magenta (CI 677) was first prepared by oxidation of crude aniline with stannic chloride, the yield was only 15%. By using nitrobenzene in presence of iron or iron salts as oxidizing agent, the yield is increased to about 50%. Pure aniline does not give a Magenta type of dye, which is only obtained by the addition of *p*-toluidine; *o*-toluidine can replace aniline, but not *p*-toluidine. These empirical facts regarding the formation of Magenta were known at an early stage and the reason became obvious when the triphenylmethane structure of the dyes was recognized, since *p*-toluidine is necessary for supplying the methane carbon atom. Magenta is now manufactured by oxidizing a mixture of aniline, *o*- and *p*-toluidine with nitrobenzene or nitrotoluene, or a mixture of the two, in the presence of anhydrous zinc chloride, ferrous chloride and ferric oxide. The temperature is raised gradually from 60° to 140°, when a vigorous exothermic reaction sets in. Heating is then stopped, and the reaction kettle spray-cooled, so that the temperature is not allowed to rise above 170° at the rate of 2° per hour. The total time of the melt is about 24 hours. The cold melt is powdered, washed with acidulated water to remove unreacted amines, the residue dissolved in acid, and the dye base precipitated with milk of lime. It is then redissolved in hydrochloric acid and crystallized; the product is a mixture of Rosaniline and Pararosaniline, the former being the major constituent.[13] The composition of the dye and the shade depend on the relative proportions of the three amines; for Crystal Fuchsine a mixture of 38% of aniline, 35 of *o*-toluidine and 27 of *p*-toluidine is employed. For conversion into the phenylated rosanilines, other proportions are used according to the required tone of the blue dyes. Homogeneous dyes of the Magenta series can be prepared by modified methods. Thus, for New Magenta (Homolka, 1889) (MLB; CI 678), a cheaper and more soluble dye than Magenta, the indicated process gives a better yield than the older method for Magenta. The various Magentas are red dyes; they are more valu-

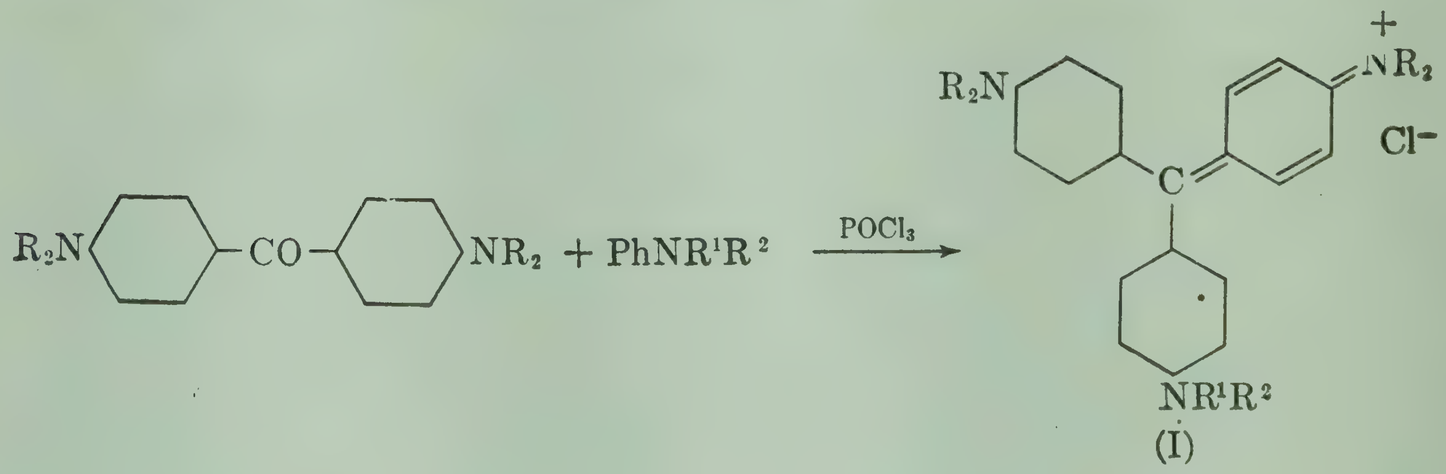


Rosaniline

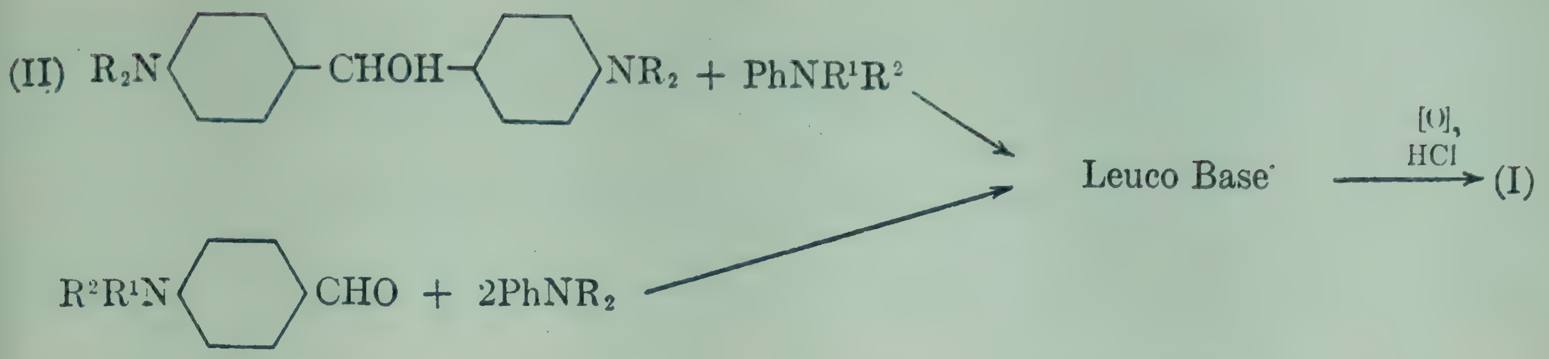


able the yellower the tone, and are frequently shaded with a yellow dye such as Auramine.

N-Alkyl Rosanilines (I). While the introduction of *C*-methyl groups in Pararosaniline makes the shades slightly bluer, *N*-methylation changes the shade to violet, the dyes becoming increasingly violet until there is a maximum of six methyl groups. With seven methyl groups the shade changes to green, and to yellow with eight.[7] *N*-Alkylated dyes of the triarylmethane series are prepared by three general methods, of which the first is most widely used. (1) Michler's ketone or its ethyl analog ("ethyl ketone") is condensed with a secondary or tertiary aromatic amine unsubstituted in the *p*-position, or with other components such as an indole, having a reactive position for attachment of the methane carbon atom. The condensing agent is phosphorus oxychloride, which

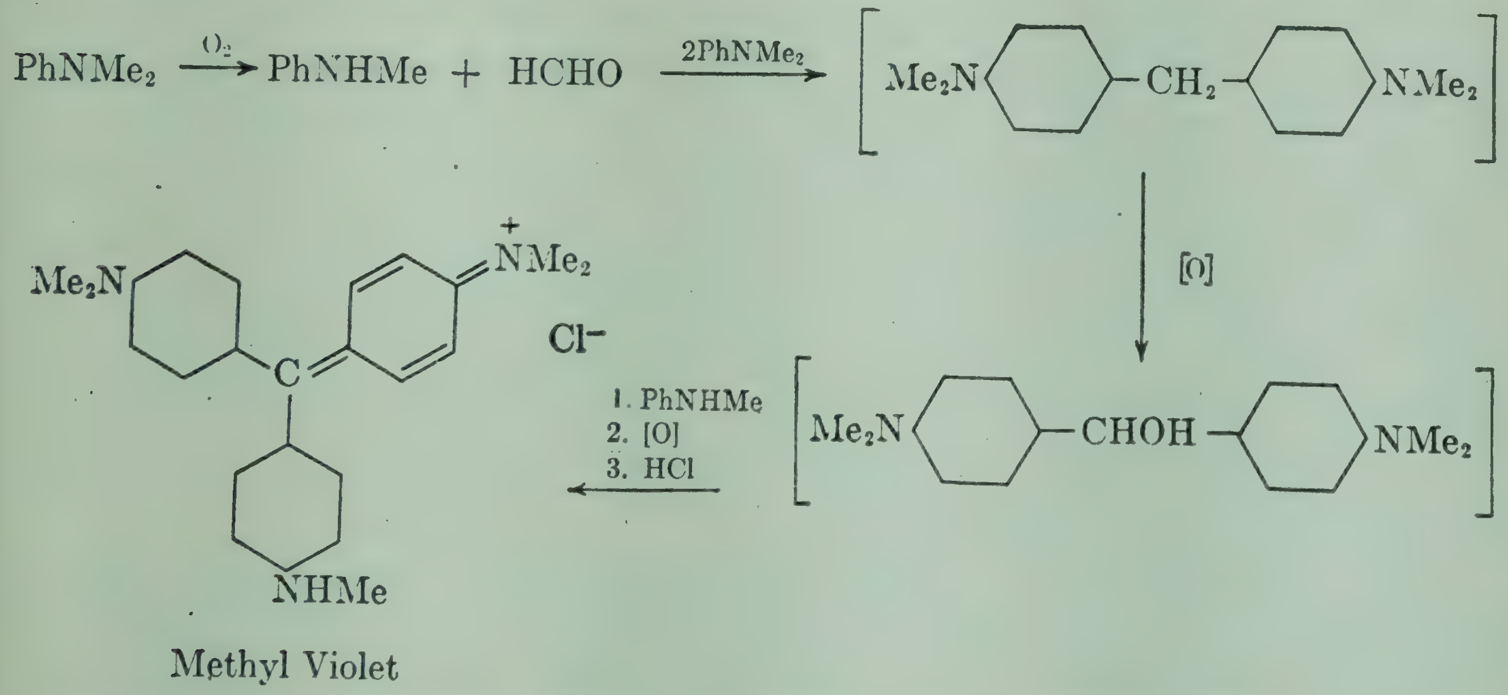


has to be used in the proportion of one mole to one mole each of the ketone and the amine since the reaction probably proceeds through the ketone dichloride (α,α-dichloromethane). (2) In the benzhydrol or carbinol process, Michler's hydrol or an analogous compound (II) is condensed with an aromatic amine in presence of sulfuric acid. (3) In the aldehyde process, which is similar to the method for making Malachite


(II) R₂N–CHOH–NR₂ + PhNR¹R²
Leuco Base
[O], HCl
(I)
R²R¹N–CHO + 2PhNR₂

Green, a *p*-aminobenzaldehyde is condensed with two moles of an aromatic amine to form the leuco base. While *N*-alkylrosanilines are thus prepared by starting with *N*-alkylanilines and carrying out the triphenylmethane condensation in various ways, direct alkylation of rosaniline has been suggested in special cases. Vinyl methyl ketone acts as an alkylating agent, giving γ-ketobutyl derivatives, and Pararosaniline for instance treated with this reagent becomes reddish blue.[32] Dyes of the Crystal Violet and Malachite Green types have been prepared by condensing *p*-bromodimethylaniline (or other *p*-halogenated tertiary amine) with an ester or ketone (e.g., diethyl carbonate, ethyl benzoate, anthraquinone) in presence of sodium.[33]

Methyl Violet (CI 680) is made by a specific method, consisting in the oxidation of dimethylaniline by air with copper sulfate as catalyst; phenol and a large amount of salt are used as diluents. The methane carbon atom is provided by oxidation of a methyl group in a molecule of dimethylaniline to formaldehyde. The main constituent of the dye ultimately obtained is pentamethylpararosaniline. Methyl Violet is made


PhNMe₂ O₂ PhNHMe + HCHO 2PhNMe₂
Me₂N–CH₂–NMe₂
[O]
Me₂N–CHOH–NMe₂
1. PhNHMe
2. [O]
3. HCl
Me₂N
NMe₂
Cl⁻
C
NHMe
Methyl Violet

on a very large scale; the annual production is estimated at three million pounds. In addition to its application in dyeing and printing, it finds extensive use in the manufacture of inks, copying pencils, typewriter ribbons and other colored materials. Methyl Violet is useful as a bluing agent for bleached wool, a minute percentage being adequate for correcting the yellow tone.

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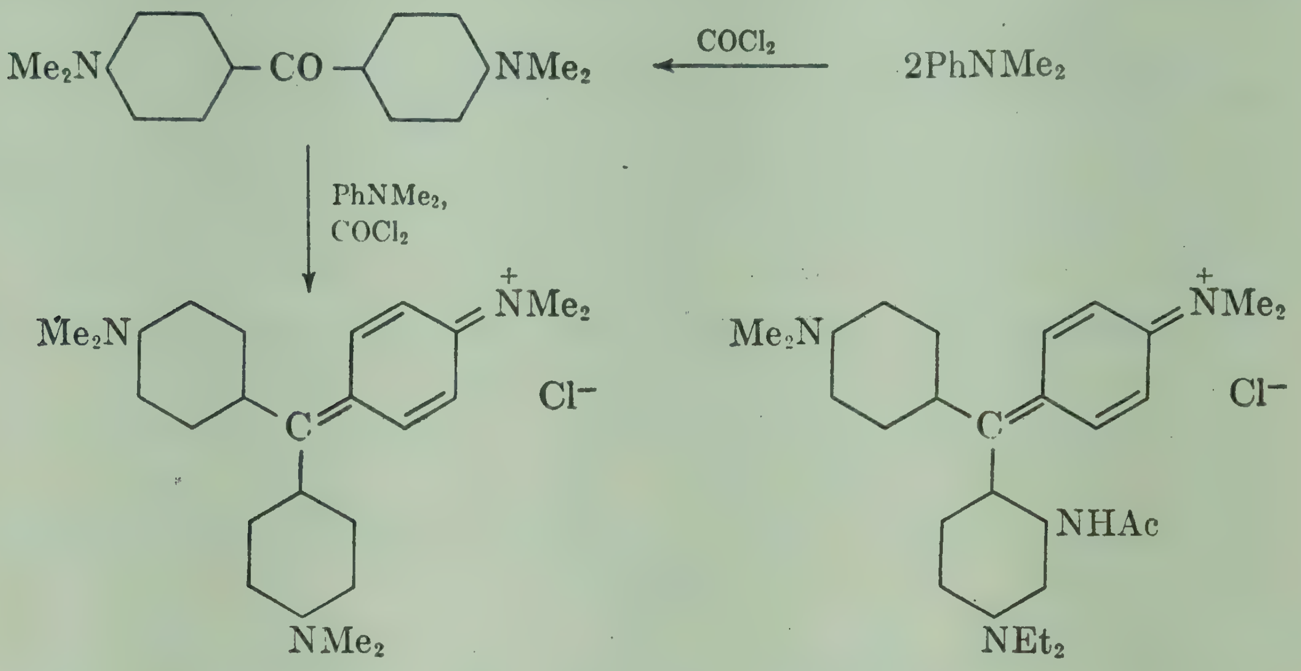
[32] IG, BP 493,154.

[33] Morton and Stevens, USP 2,029,830.

Crystal Violet (CI 681), which is a homogeneous hexamethylpararosaniline made by the phosgene process, is also largely used; its annual production is about a third of that of Methyl Violet. The preparation of leuco Crystal Violet from dimethylaniline and carbon monoxide at high pressure in presence of ferric and aluminum chloride has been reported.[34] The ethyl analog of Crystal Violet is Ethyl Violet (BASF; CI 682). Crystal Violet 10B (IG) is the condensation product of Michler's ketone and dimethyl-*m*-toluidine.[2] Brilliant Rhoduline Blue R (IG) is prepared by condensing Michler's hydrol with *m*-acetamidodiethylaniline in presence of sulfuric acid, and oxidizing the leuco base with lead peroxide, acetic acid and hydrochloric acid.[10]



Crystal Violet

Brilliant Rhoduline Blue R

When Methyl Violet is heated with methanol and hydrochloric acid under pressure, the product is Methyl Green (Monnet and Reverdin, 1874) (CI 684), which is a basic dye with somewhat better fastness to light than Malachite Green; but the latter dye has nevertheless displaced Methyl Green entirely. Methyl Green has some use as a stain in bacteriological and histological work.

By the interaction of primary amines with vinyl methyl ketone, *N*-butanonyl groups are introduced ($RNH_2 + CH_2{=}CH{-}COCH_3 \rightarrow RNHCH_2CH_2COCH_3$). IG have studied this reaction on basic dyes, and it is reported that brightness, solubility and affinity (fiber not mentioned) are thus improved. An example is Fuchsine Violet V 651, the mono-*N*-butanonyl derivative of Pararosaniline.[35] The introduction of

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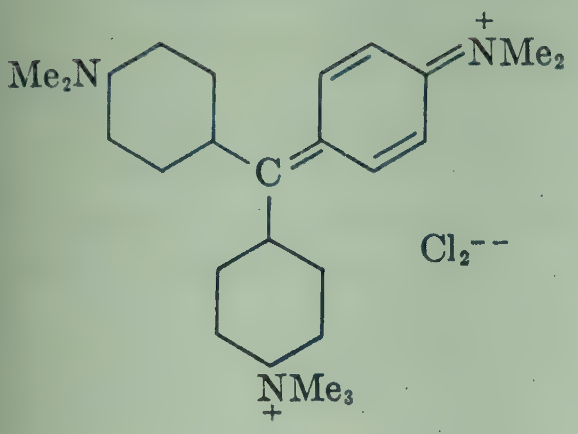
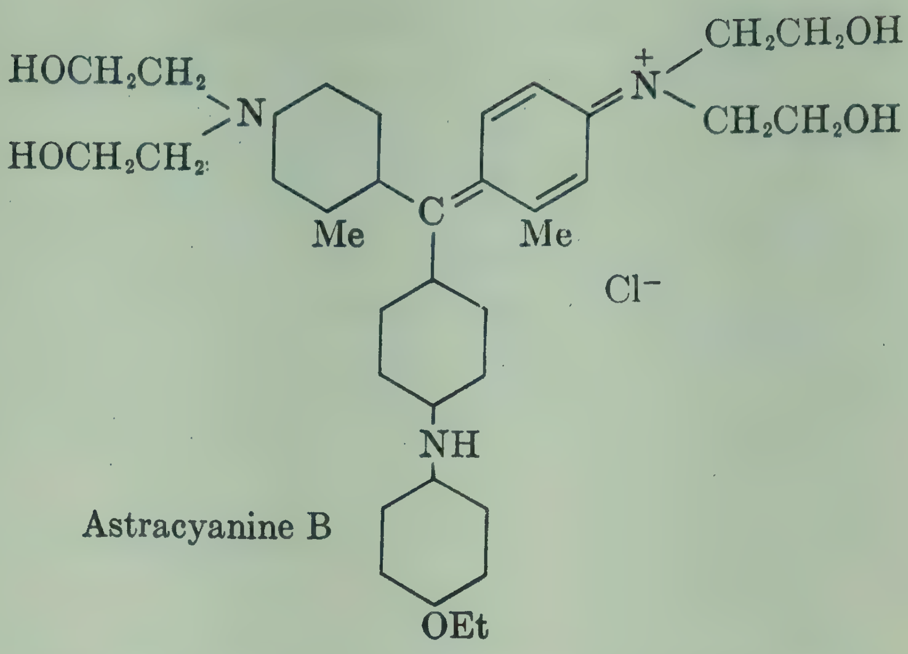
[34] Liston and Dehn, *Ind. Eng. Chem.* **26**, 1073 (1934).

[35] *FIAT* **1313**, III.



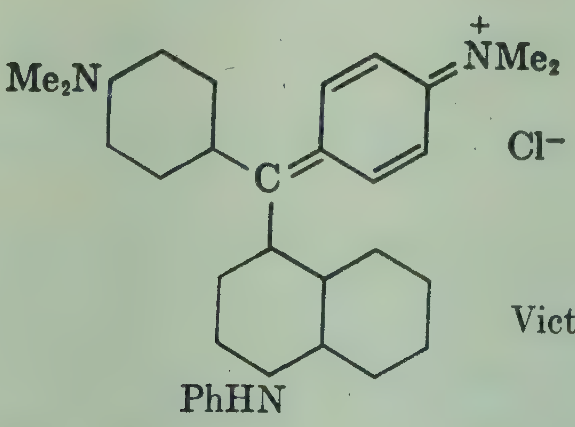
Methyl Green



Astracyanine B

hydroxy or alkoxy substituents in the alkyl groups and the replacement of an alkyl by an aryl group are modes of improving the fastness properties; a *p*-anisidino- or *p*-toluidino group gives dyes of better light fastness. Astracyanine B (IG) is made by condensing *p*-chlorobenzaldehyde with bis-β-hydroxyethyl-*m*-toluidine in a slightly acid (sulfuric acid) medium at 100°; making alkaline with ammonia and separating the resinous leuco base; oxidizing with dichromate, hydrochloric acid and oxalic acid; heating the color base with *p*-phenetidine, dissolving the dye in acidified water and salting out.[10]

A series of valuable blue dyes are obtained by replacing one of the alkylaniline residues in *N*-alkyl Rosanilines by an *N*-alkyl- or phenylnaphthylamine. An example is the important dye, Victoria Blue B (Caro and Kern, 1883) (BASF; CI 729), made by condensing Michler's hydrol with phenyl-α-naphthylamine, and then oxidizing; or preferably by condensing Michler's ketone with phenyl-α-naphthylamine in presence of phosphorus oxychloride. The latter method represents an important general procedure for the preparation of such triphenylmethane dyes. It is not necessary to isolate Michler's ketone; two moles of dimethylaniline or diethylaniline (actually employed in about 35% excess, which

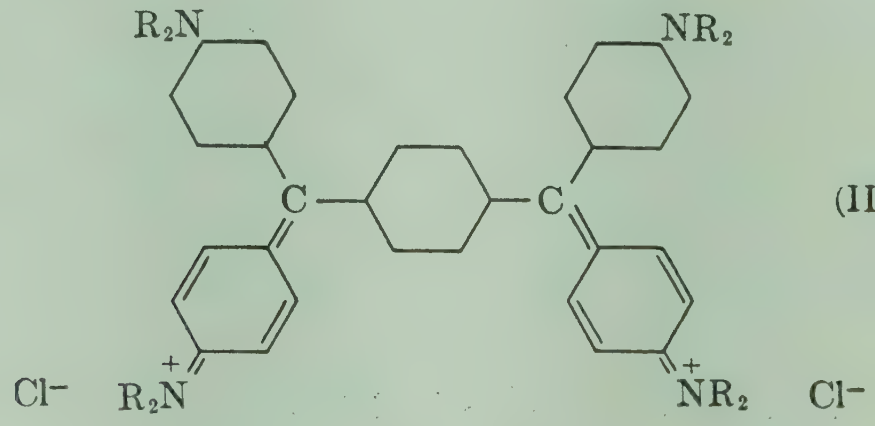


Victoria Blue B

is recovered later) are condensed with phosgene in presence of zinc chloride to form the ketone, a solvent (e.g., toluene) is added, and the second stage of the reaction is then carried out by adding a mole of the appropriate amine and phosphorus oxychloride. The first or phosgene stage is a slow reaction, carried out over several days with a stepwise increase of temperature. The second stage proceeds rapidly and is completed by a few minutes heating at 100° after the phosphorus oxychloride has been run in. After partial neutralization with caustic soda, toluene is recovered; the dye separates as a tar from which impurities are removed by digestion with xylene, and further purification is effected by dissolving in hydrochloric acid and salting out. The dye again separates as a moist tar, which is dried down and powdered.[2]

Victoria Blue R (By; CI 728) is the analog from ethyl-α-naphthylamine, and 4R (BASF; CI 690) from phenyl-methyl-α-naphthylamine. Victoria Pure Blue BO (IG) is from "ethyl ketone" and ethyl-α-naphthylamine.[2] The Victoria Blues are largely used in calico printing and in wool and silk dyeing for the beauty of the sky blue to royal blue shades, although the light fastness is poor. On wool the fastness to milling and stoving is good.

IG claim that blue-black to green-black dyes are obtained when aromatic polyaldehydes, e.g., terephthalaldehyde, or substances which react like aromatic dialdehydes (e.g., ω, ω, ω′, ω′-tetrachloro-*p*-xylene) are condensed with secondary or tertiary aromatic amines and the leuco compounds oxidized in the presence of mineral acids.[36] Such deep shades have not so far been obtained with basic dyes of the triphenylmethane class; on the other hand it has been stated that by condensing terephthaloyl chloride with dimethyl- or diethylaniline bistriphenylmethane



(III)

dyes (III) are produced which are somewhat yellower in shade than Malachite Green.[37]

Phenylated Rosanilines, mentioned later, have no technical interest as basic dyes, but their sulfonic acids are valuable acid colors. An interesting reaction in this connection is the condensation of Pararosaniline with 1-chloro-2,4-dinitrobenzene to give 4,4′-diamino-2″,4″-dinitrophenylfuchsonimide.[38] When the nitro groups are reduced, the products dye wool, silk or tannin-mordanted cotton in fast violet shades.

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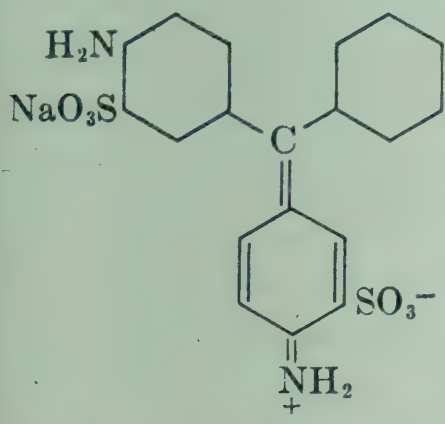
[36] BP 432,204.

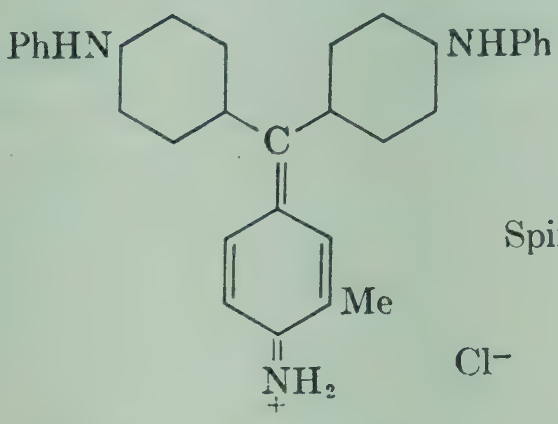
[37] Bogert and Nisson, *Proc. Natl. Acad. Sci.* **10**, 421 (1924).

ACID DYES OF THE MAGENTA SERIES

Acid dyes can be obtained from Magenta by treatment with fuming sulfuric acid until the product is soluble in water; this gives a mixture of di- and trisulfonic acids; since Magenta is usually a mixture of homologs, so is Acid Magenta. However, the important constituent is trisulfonated Pararosaniline.

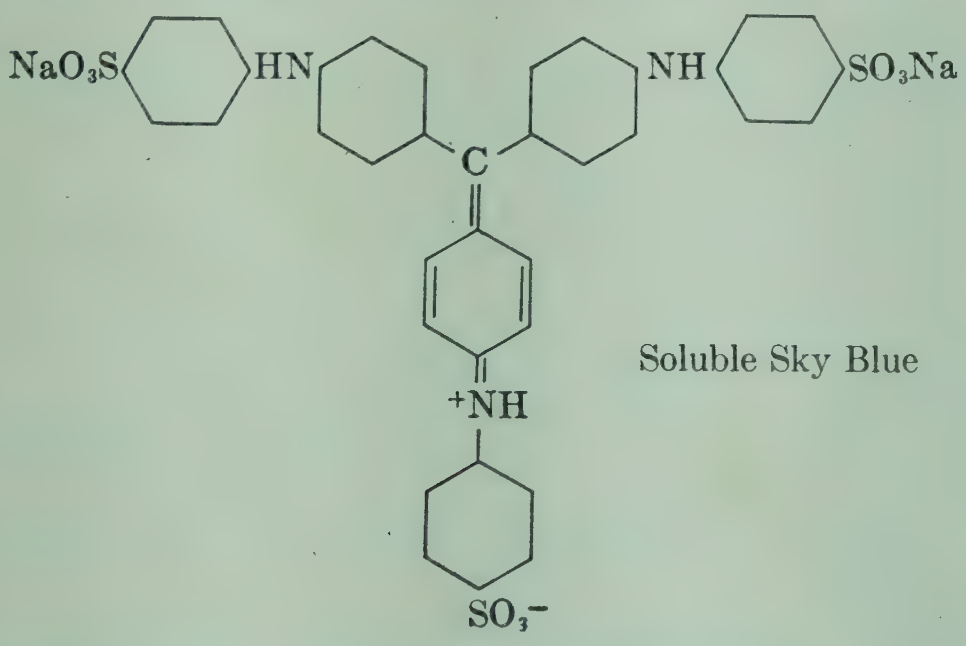


Acid Magenta



Spirit Blue

Sulfonic acids of phenylated Rosanilines, which are old dyes (Nicholson Blue, Soluble Blue, Water Blue, Alkali Blue; CI 703–707), continue to be extensively used. Phenylated Rosanilines are obtained by heating salts of Rosaniline with aniline; the monophenyl compound is reddish violet, the diphenyl bluish violet, and the triphenyl blue. Aniline Blue or Spirit Blue (CI 689), obtained by heating Magenta with aniline in presence of a little benzoic acid, is mainly a diphenyl derivative; the *o*-toluidine residue does not undergo *N*-phenylation. Thus New Magenta cannot be phenylated by this method, while Pararosaniline can be triphenylated without difficulty. The redness or blueness of the shades of these phenylated Rosanilines is controlled by the degree of phenylation,



Soluble Sky Blue

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[38] Poraĭ-Koschitz and Mandel'schtam, *J. Gen. Chem. U.S.S.R.* **4,** 842 (1934).

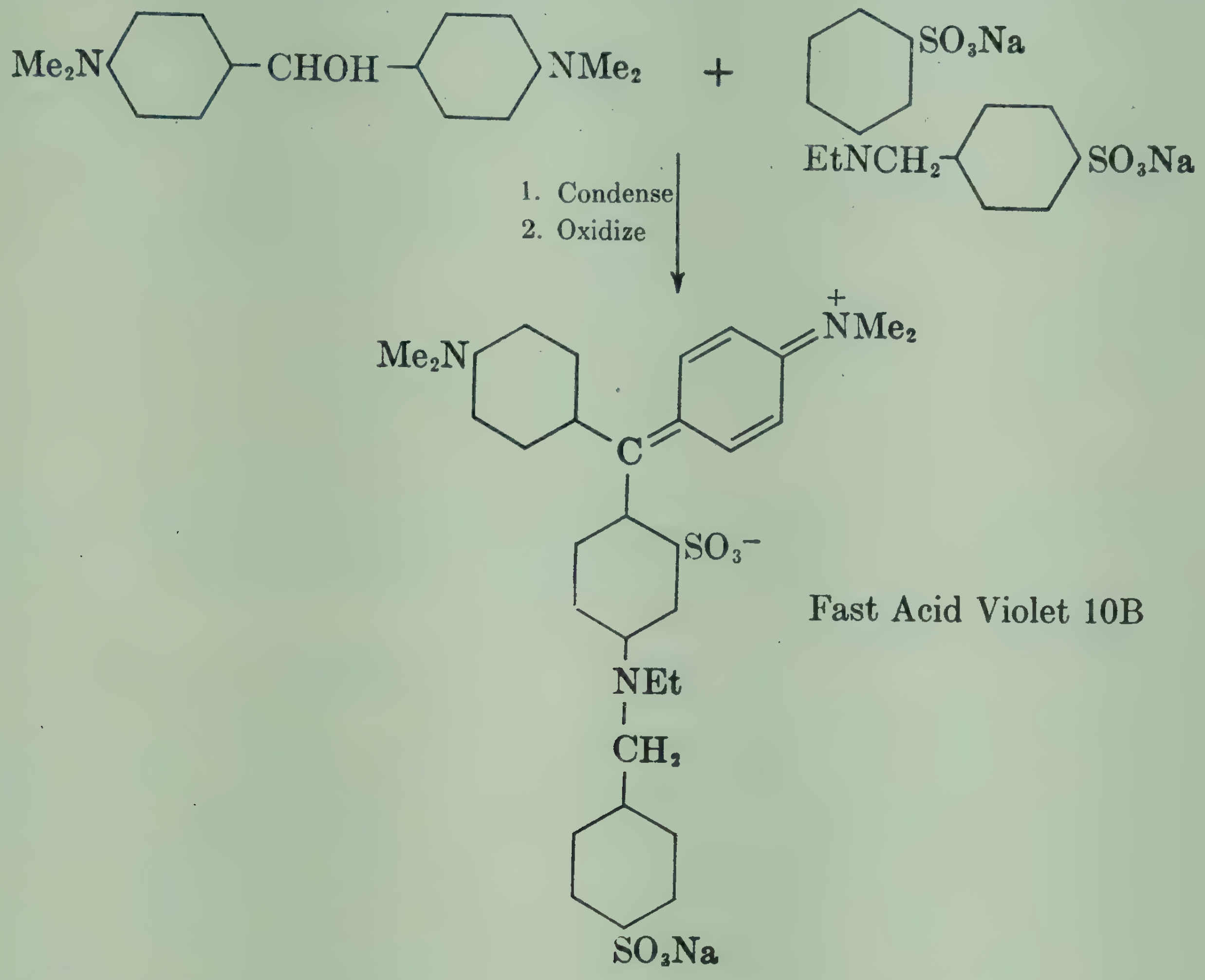
and by using *o*-toluidine, which gives redder shades, in place of aniline. They are alcohol-soluble, and were used at one time for coloring spirit varnishes, but they are now made merely as intermediates for the acid dyes produced by sulfonation. They become readily soluble by sulfonation to mono-, di- and trisulfonic acids. The sulfonic groups apparently enter the new benzene rings introduced by phenylation, since the Rosanilines themselves are difficult to sulfonate. By warming Aniline Blue with concentrated sulfuric acid until the product is soluble in sodium carbonate solution, a monosulfonic acid, Alkali Blue (CI 704), is obtained. It dyes wool from an alkaline bath; the colorless carbinol is absorbed, and the color is developed by subsequent acid treatment. When the sulfonation of Aniline Blue is continued till the product is water-soluble, the trisulfonic acid is formed; this is Soluble Blue (CI 705), used in dyeing wool, and in blueing paper and bleached cotton materials. Soluble Sky Blue (Sandmeyer, 1892) (Gy; CI 706) is a homogeneous trisulfonic acid of triphenyl Pararosaniline, prepared by the condensation of diphenylamine-4-sulfonic acid with the required benzhydrol disulfonic acid. The Ink Blues[10] are also sulfonic acids of phenylated Rosanilines; the sulfonation products are given a lime treatment, the soluble calcium salts are decomposed with sulfuric acid and the free sulfonic acids are ground up with sodium sulfate. Reflex Blue AG (IG) is prepared by heating Pararosaniline (460 parts), aniline (2400) and benzoic acid (8.5) for one hour at 180–182°. Excess aniline is distilled off *in vacuo*, and the residue sulfonated by treatment with five times its weight of concentrated sulfuric acid at 25° until the product is soluble in hot 3% ammonia.[2] Other brands of Reflex Blue such as AGG, B, 2G, 8G, K, 8K, RB and TBK (IG) are prepared by varying the proportion of aniline or the conditions of sulfonation, and by using *o*-toluidine or *m*-toluidine in place of aniline.[10, 28] Reflex Blue AGG and Reflex Violet A are used for printer's ink.

A route to phenylated Rosanilines is to heat a diaminotriphenylmethane containing a *p*-chlorine atom in the third benzene ring with an arylamine (e.g., *p*-phenetidine); when the diaminotriphenylmethanes are prepared from *m*-2-xylidine, the acid dyes ultimately produced by sulfonation of the N-phenylrosaniline derivatives dye clear shades with good light fastness.[39]

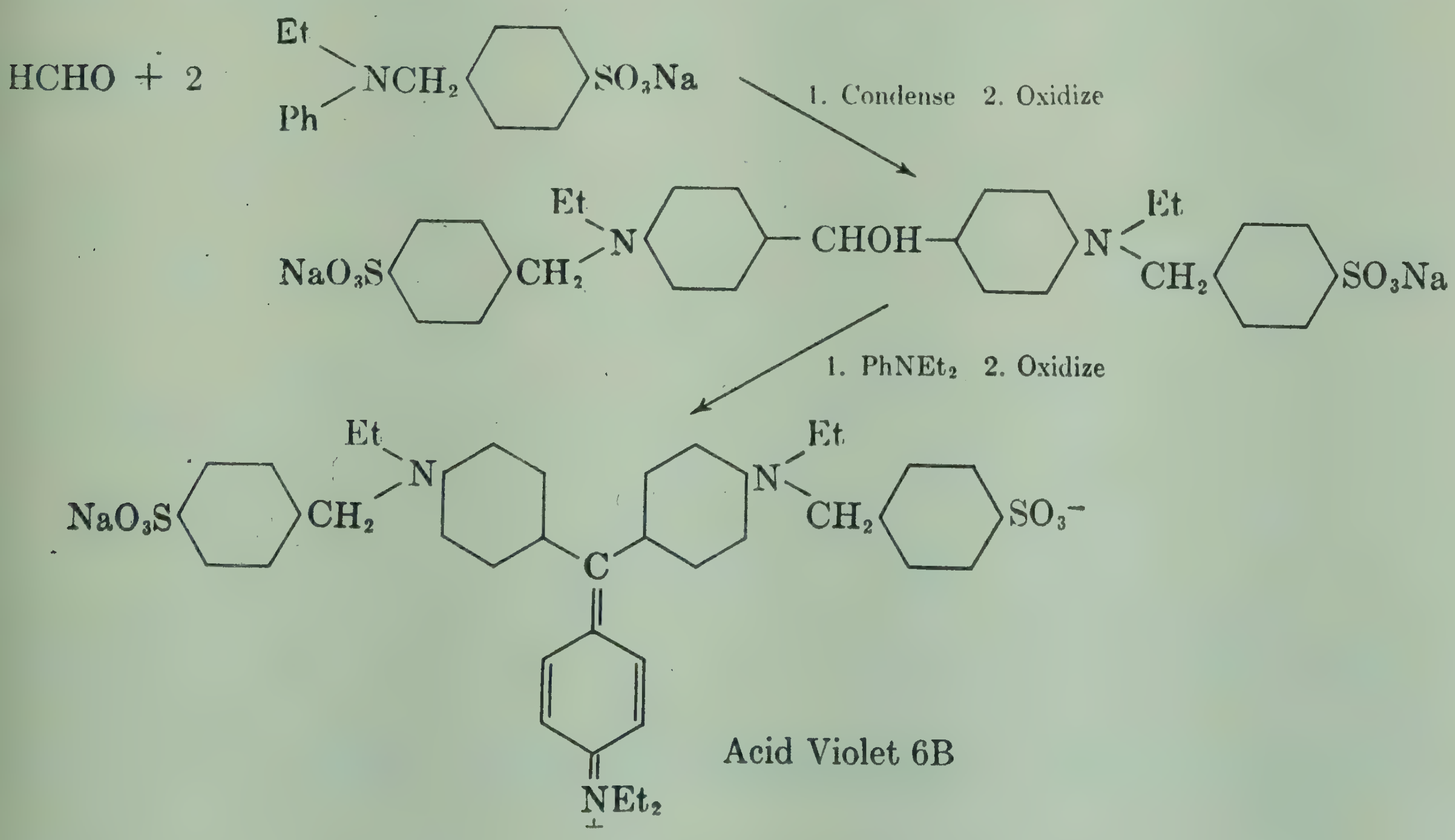
The sulfonation of Methyl Violet or Crystal Violet to form Acid Violets does not proceed satisfactorily, and the device of introducing benzyl groups is usually adopted. The sulfonic group may be present in the benzylated intermediate, or a benzylrosaniline may be subsequently sulfonated. The obvious advantage of the first method is that the number and position of the sulfonic groups are definite and pre-

[39] IG, BP 520,968.

determined, and it is employed for the preparation of Fast Acid Violet 10B (Hassenkamp, 1891) (By; CI 696) and a series of similar and largely used dyes. Acid Violet BW (IG) is made from Michler's hydrol and benzylaniline disulfonic acid, prepared by sulfonating *N*-benzylorthanilic acid.[10] Acid Violet 6B (Sandmeyer, 1890) (Gy; CI 698) (Formyl Violet S4B, C) illustrates a variation of the procedure in which the benzhydrol contains the requisite sulfobenzyl groups. Brilliant Wool Blue FFR

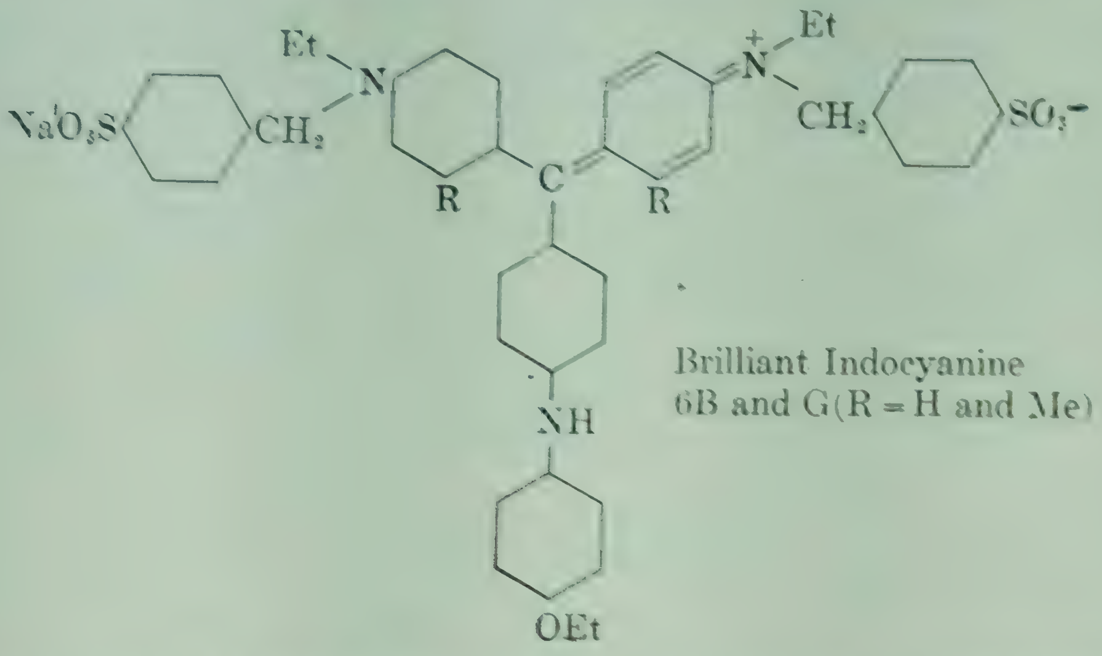

Me₂N
CHOH
NMe₂
+
SO₃Na
EtNCH₂
SO₃Na
1. Condense
2. Oxidize
Me₂N
+
NMe₂
C
SO₃⁻
NEt
CH₂
SO₃Na

Fast Acid Violet 10B

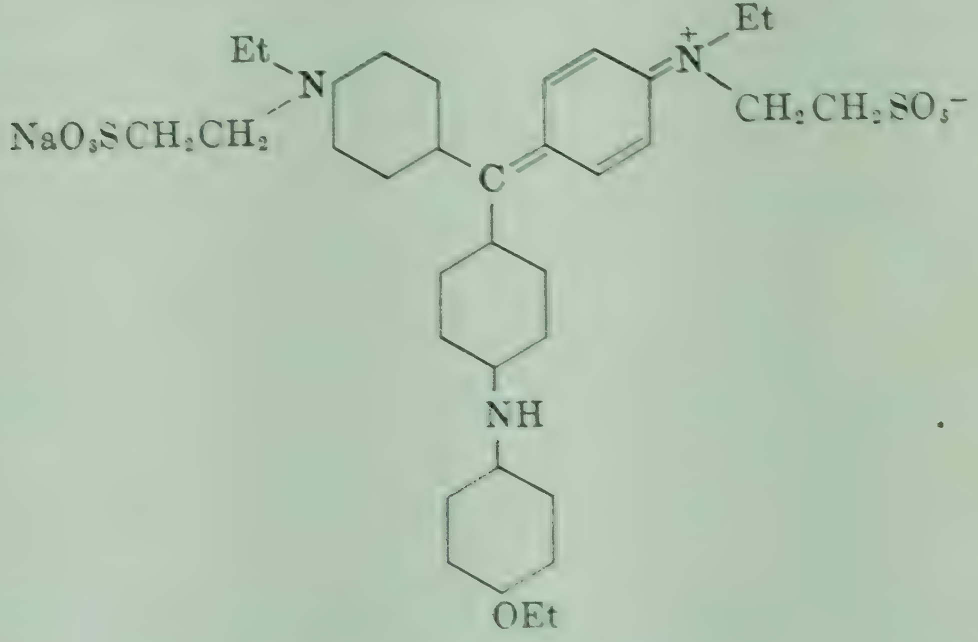

HCHO + 2
Et
NCH₂
Ph
SO₃Na
1. Condense 2. Oxidize
NaO₃S
CH₂
Et
N
CHOH
N
Et
CH₂
SO₃Na
1. PhNEt₂ 2. Oxidize
NaO₃S
CH₂
Et
N
C
Et
N
CH₂
SO₃⁻
NEt₂
+

Acid Violet 6B

(By, 1900) is made by condensing *p*-diethylaminobenzaldehyde with two moles of *N*-ethyl-*N*-*p*-sulfobenzyl-*m*-toluidine. Wool Blue 5B (IG) is a similar dye prepared from 2-chloro-4-diethylaminobenzaldehyde and two moles of *N*-ethyl-*N*-*p*-sulfobenzylaniline.[40] These dyes have very poor light fastness.


Brilliant Indocyanine 6B and G(R = H and Me)

Recent IG introductions of this type are Brilliant Indocyanine 6B (1927) and G (1928) (ST Erg I 775a); the latter dye is faster to alkali. The replacement of sulfobenzyl groups by sulfoethyl groups in Brilliant Indocyanine 6B gives the dye Brilliant Wool Blue FFRL extra.[28] Acid Brilliant Blue R extra is another dye in which the sulfonic groups are attached to aliphatic carbon atoms.[10] It is prepared by condensing *p*-diethylaminobenzaldehyde with two moles of ethyl-*m*-tolyltaurine, and oxidizing the leuco compound with dichromate, oxalic acid and sulfuric


Brilliant Wool Blue FFRL extra

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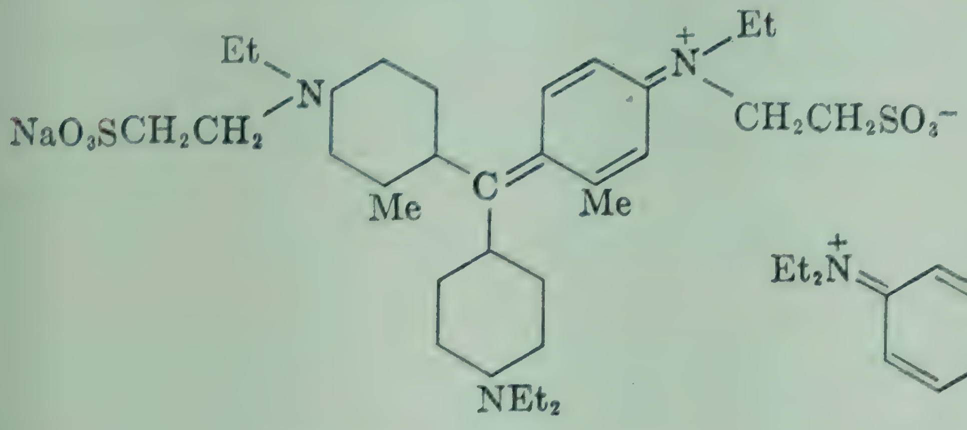
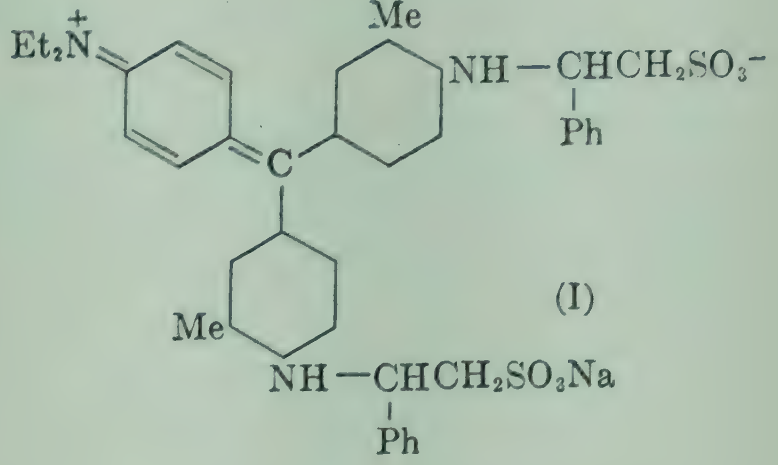
[40] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935.

acid. Another method of introducing sulfonic groups in the side-chain is to use intermediates such as β-sulfo-α-phenylethyl-*o*-toluidine, prepared by adding chlorosulfonic acid to styrene and condensing the product with *o*-toluidine. The usual reactions with *p*-diethylaminobenzaldehyde then yield the dye (I), which is very similar to the old Formyl Violet type except for the position of the sulfonic groups.[41] Other intermediates which may be used for this type of dye are *o*-sulfomethylphenyltaurine, *o*-xylene-ω,ω′-disulfonic acid, and β-sulfoethylbenzene.[42] Another method of introducing sulfoalkyl groups into a triphenylmethane dye is to treat a dye already containing at least one sulfatoalkylamino group with sodium sulfite at about 150° under pressure, the $N-C_2H_4-O-SO_3H$ group being converted into $N-C_2H_4-SO_3H$. Instead of employing the dyestuff as the starting material, an intermediate, e.g., a leuco compound, containing a sulfatoalkylamino group may be used for this reaction and the product afterwards converted into the dyestuff.[43] As a result of activity in the detergent field, glycerol derivatives (e.g., $Ph-NBu-CH_2-CHOH-CH_2SO_3H$) and numerous other intermediates of similar type have been suggested.[44] The same devices can also be adopted for afterchrome dyes derived from fuchsone which are described later.[45]


Acid Brilliant Blue R extra


(I)

The old and still highly valued diphenylamine derivative, Acid Violet 6BN (Müller, 1891) (BASF; CI 717) does not contain benzyl groups, and it is made by sulfonating the condensation product of Michler's ketone and 3-ethoxy-4′-methyldiphenylamine.[2] Alkali Violet 6B (BASF; CI

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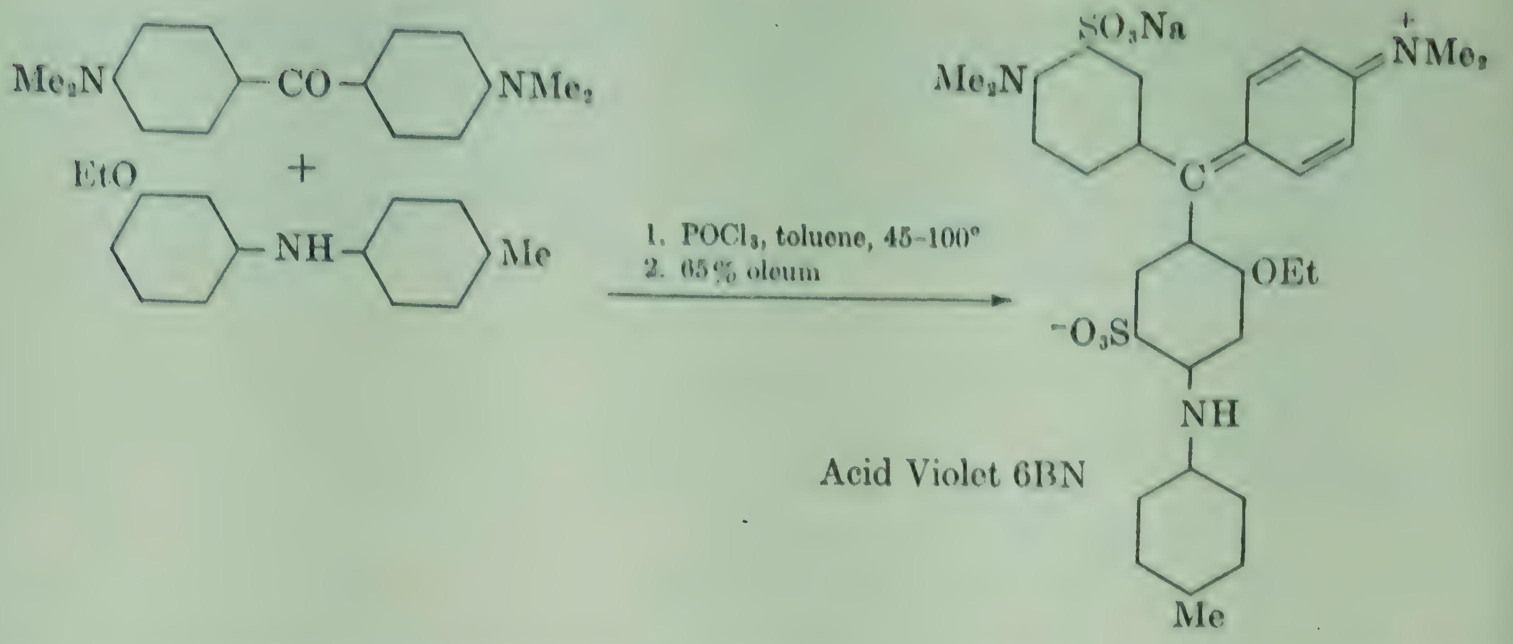
[41] IG, BP 469,443.

[42] IG, BP 447,067.

[43] IG, BP 420,307.

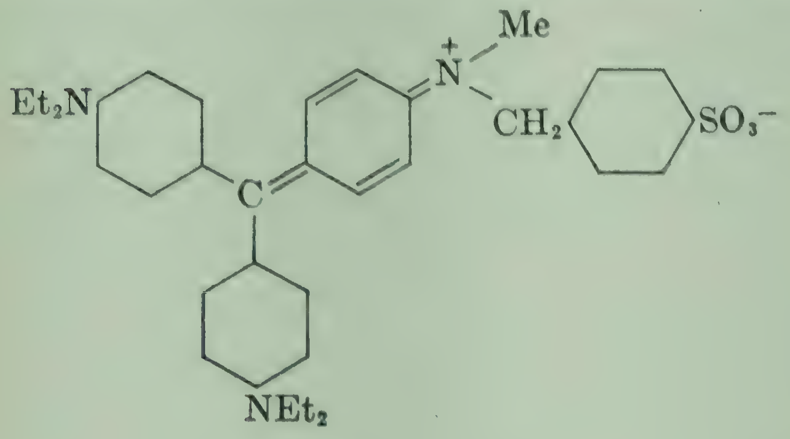
[44] IG, GP Anm. I. 46,110.

[45] IG, BP 472,407.

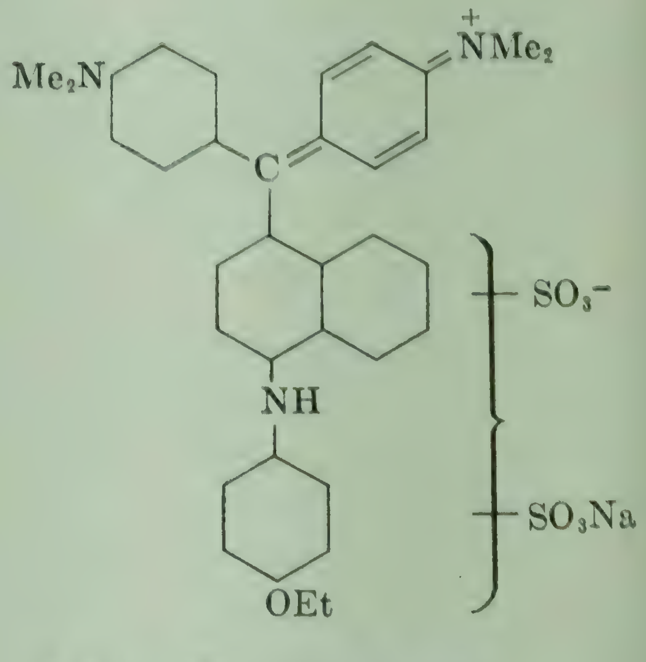

Me₂N
CO
NMe₂
EtO
+
NH
Me
1. POCl₃, toluene, 45-100°
2. 65% oleum
SO₃Na
Me₂N
NMe₂
C
OEt
⁻O₃S
NH
Me

Acid Violet 6BN

700) is another diphenylamine derivative, prepared similarly by condensing "ethyl ketone" with *N*-methyldiphenylamine and then sulfonating. The position of the sulfonic groups in these dyes is uncertain. Alkali Violet 4BN and 3R contain benzyl groups, but they are prepared by ultimate sulfonation; for the 3R brand the intermediates are Michler's ketone and *N*-benzyl-*o*-toluidine, and after the usual phosphorus oxychloride condensation the product is sulfonated with 30% oleum.[2]


Et₂N
C
N
Me
CH₂
SO₃⁻
NEt₂

Alkali Violet 4BN

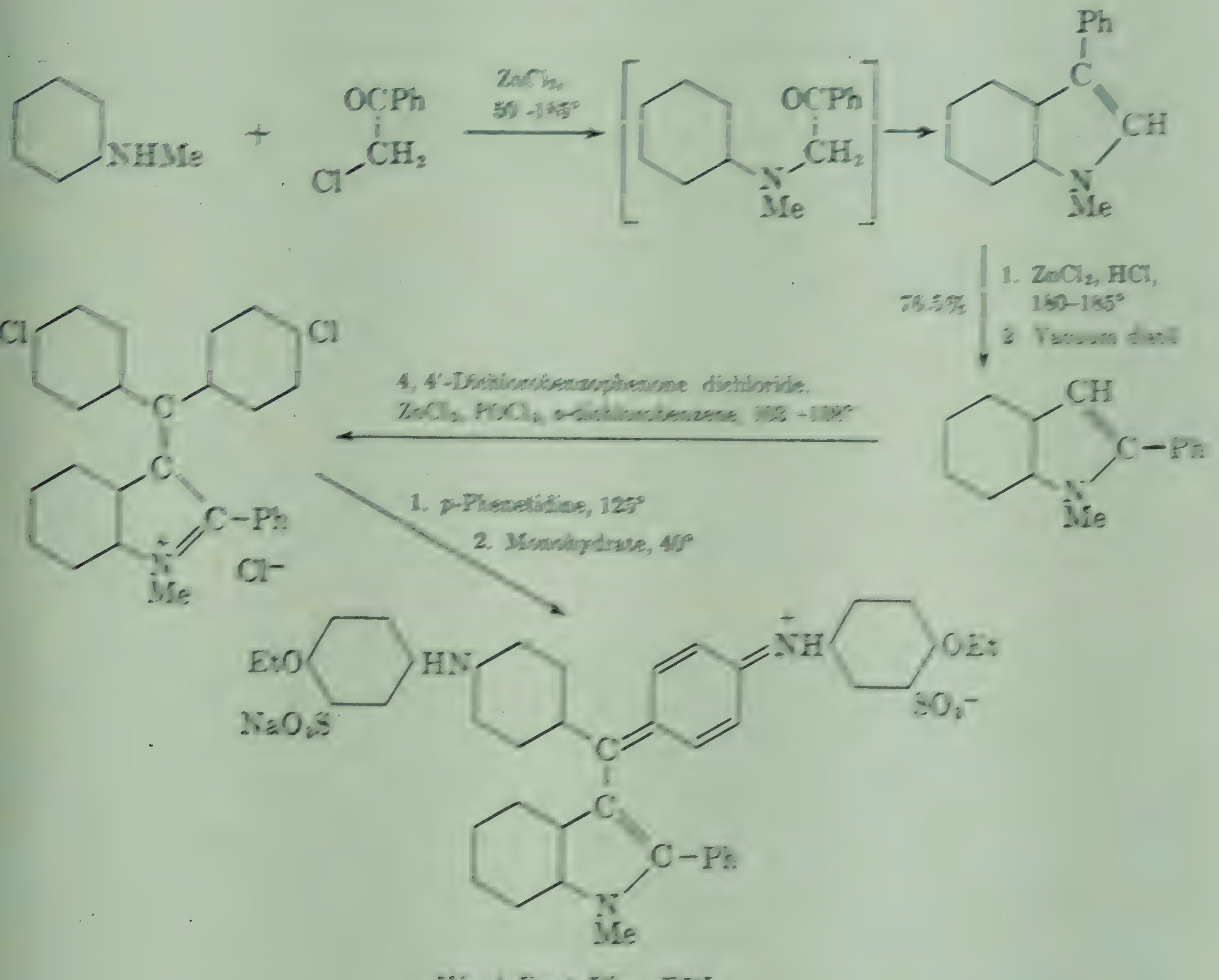

Me₂N
NMe₂
C
SO₃⁻
NH
SO₃Na
OEt

Brilliant Wool Blue G extra

Brilliant Wool Blue G extra (IG) and Wool Blue N extra (IG) are both prepared by sulfonation of the basic dye obtained by the condensation of Michler's ketone with *p*-ethoxyphenyl-α-naphthylamine; the *p*-tolyl-α-naphthylamine analog is Wool Blue R extra (IG). Wool Blue G extra (IG) is prepared by sulfonation of the basic dye obtained by condensing Michler's ketone with 1,2′-dinaphthylamine.[2, 10] Cyanol Silk Blue B (IG) is prepared by the manganese dioxide-sulfuric acid oxidation of a mixture of 4,4′-bis-diethylaminodiphenylmethane and 1-naphthylamine-2,4,7-trisulfonic acid.[11]

Indole derivatives. Wool Fast Blue FBL (IG) is an interesting triarylmethane dye in which one of the aryl residues is 1-methyl-2-phenylindole, prepared from monomethylaniline and ω-chloroacetophenone. The preparation of the dye involves a method not usually adopted for the triphenylmethane dyes. Instead of the required *N*-substituted diaminobenzophenone or -benzhydrol, dichlorobenzophenone dichloride is used for the condensation with the indole and the chlorine atoms are subsequently replaced by arylamino groups. Wool Fast Blue FGL (IG) is a similar dye from 1-*iso*butyl-2-(*p*-chloro)phenyl-4,6-dimethylindole, which is difficult to prepare; production of the dye was therefore abandoned.[2, 11] By using suitable arylamines for replacing the chlorine atoms in this synthesis, green and violet dyes can be produced.[44] Brilliant Rhoduline Violet R (IG) is stated to be the condensation product of Auramine G with a methylindole.[2] These indole derivatives have good light fastness. Another method of synthesis starts with a substituted

CHART 2
Preparation of Wool Fast Blue FBL


NHMe
+
OCPh
CH₂
Cl
ZnCl₂,
50–185°
OCPh
CH₂
N
Me
Ph
C
CH
N
Me
78.5%
1. ZnCl₂, HCl,
180–185°
2. Vacuum distil
CH
C–Ph
N
Me
4, 4'-Dichlorobenzophenone dichloride.
ZnCl₂, POCl₃, o-dichlorobenzene, 102–108°
Cl
Cl
C
C
C–Ph
N
Me
Cl⁻
1. p-Phenetidine, 125°
2. Monohydrate, 40°
EtO
NaO₃S
HN
C
NH
OEt
SO₃⁻
C
C–Ph
N
Me

Wool Fast Blue FBL

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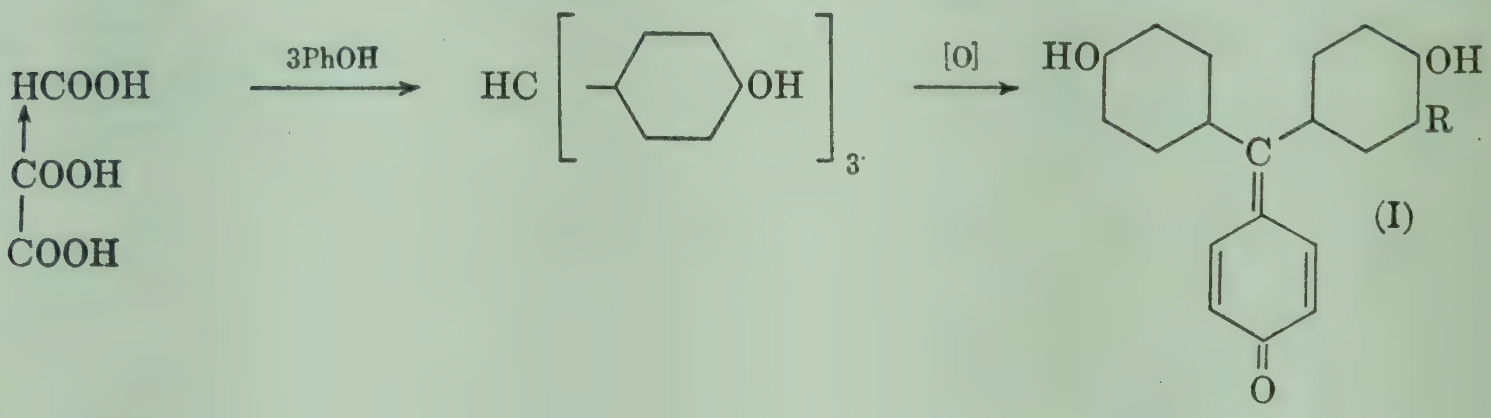
[44] Groves and IG, BP 496,580; 496,657.

benzoic acid or indole-3-carboxylic acid.[47] Thus 4-ethoxy-*N*-methyldiphenylamine-4′-carboxylic acid is condensed with 2 moles of a suitable indole, or with 1 mole each of two different indoles; the products when sulfonated yield blue acid dyes of high light fastness; an example is Wool Fast Blue 1736 (IG) for which two moles of 1,2-dimethylindole are used.[2, 47] As well as the usual indoles, *N*-ethylcarbazole and *N*-cyanoethylcarbazole may be used. By starting with 2-phenyl-*N*-methylindole-3-carboxylic acid, triindolylmethane dyes are obtained. Other examples of indolyl derivatives and methods for their preparation are described in IG patents.[48]

Rosolic Acid (Fuchsone) Series

Rosolic Acid or Aurine (CI 724), one of the oldest synthetic dyes, was made by the oxidation of crude phenol. It was therefore the phenolic counterpart of Magenta, and consisted essentially of a mixture of two homologs, of which the main constituent was the *o*-cresol derivative



(I)

Aurine (R = H)

(I; R = Me). The methane carbon atom for the triphenylmethane dye is provided by the *p*-cresol present in the crude phenol. A homogeneous product, sometimes called Aurine or Corallin to distinguish it from Rosolic Acid, the higher homolog, was made later by heating a mixture of phenol, oxalic acid and concentrated sulfuric acid. Rosolic Acid and Aurine are red spirit-soluble dyes which were used at one time for coloring lacquers and varnishes, and the Turkey Red colored lakes were used for printing wall paper; but they are toxic compounds and have been superseded by better dyes. Their only interest now is as indicators in alkalimetry.[49] The technically important dyes of the series are salicylic acid derivatives. Chrome Violet (Sandmeyer, 1889) (Gy; CI 727) is made by heating salicylic acid and formaldehyde in presence of concentrated sulfuric acid and a little sodium nitrite as oxidizing agent; it is a valuable chrome-mordant dye for calico printing, although the reddish violet shades are not fast to light. Chrome Garnet B (Alioth and Bodmer, 1921) (DH; ST 847), which has two salicylamide in place of salicylic acid residues, has better fastness properties. Analogous dyes, containing only two salicylic acid residues and prepared by condensing two moles of a salicylic acid derivative with one of a benzaldehyde derivative, are useful chrome-mordant dyes for wool. Thus Eriochrome Azurol B (Conzetti, 1906) (Gy; CI 720), prepared by the oxidation of the condensation product of 2,6-dichlorobenzaldehyde and *o*-cresotinic acid, dyes wool a bordeaux shade converted into pure blue by afterchroming. Eriochrome Cyanine R (Gy; CI 722), prepared similarly from *o*-cresotinic acid and benzaldehyde-*o*-sulfonic acid, gives violet-blue shades on chroming. The chromium complex, prepared by heating Eriochrome Azurol B with the chromium ammonium salt of salicylic acid, dyes blue both on animal and cellulose fibers.[50]

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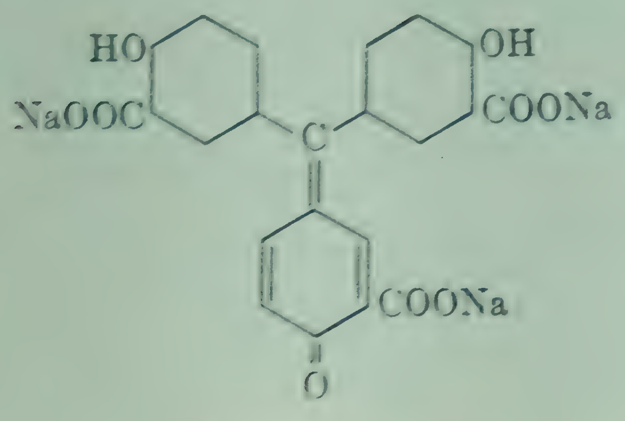
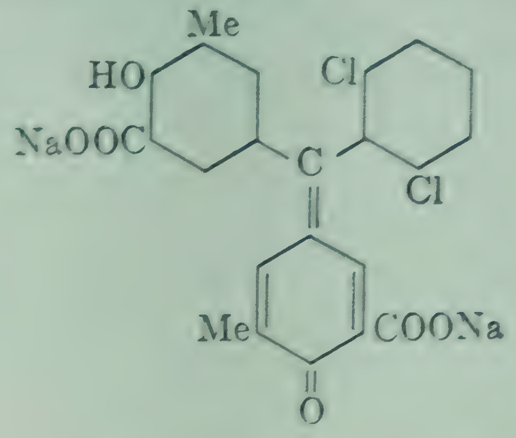
[47] IG, BP 506,679.

[48] IG, BP 417,014; 428,468; 438,426; 438,437; 439,815; 451,937.

[49] The preparation and transformations of hydroxyfuchsone (benzaurin) and of hydroxymethoxyfuchsones have been recently investigated by Ioffe, *J. Gen. Chem. U.S.S.R.* **17**, 1359; 1688 (1947); **20**, 158 (1950).

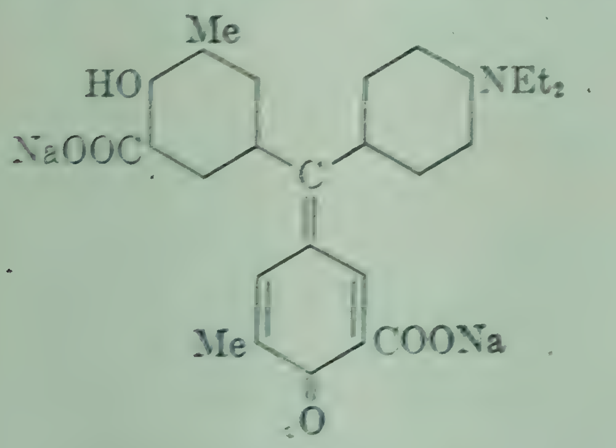


Chrome Violet

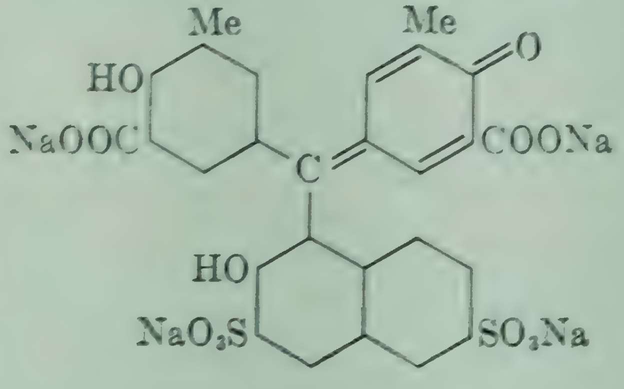


Eriochrome Azurol B

Several of the Chromoxane dyes (IG), which are acid-mordant colors developed by afterchroming, belong to this group.[10, 28] Chromoxane Brilliant Violet RE is prepared by condensing *p*-diethylaminobenzaldehyde with two moles of *o*-cresotinic acid in presence of sulfuric acid and oxidizing the leuco compound by nitrous acid. For the preparation of Chromoxane Blue R, *o*-cresotinic acid is first condensed with formaldehyde to form the diphenylmethane derivative, oxidized to the hydrol,



Chromoxane Brilliant Violet RE



Chromoxane Blue R

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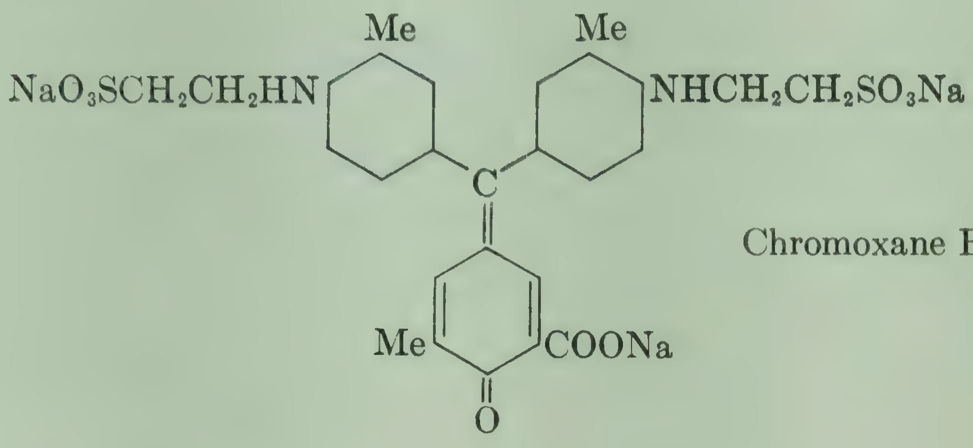
[50] Geigy, BP 560,787.

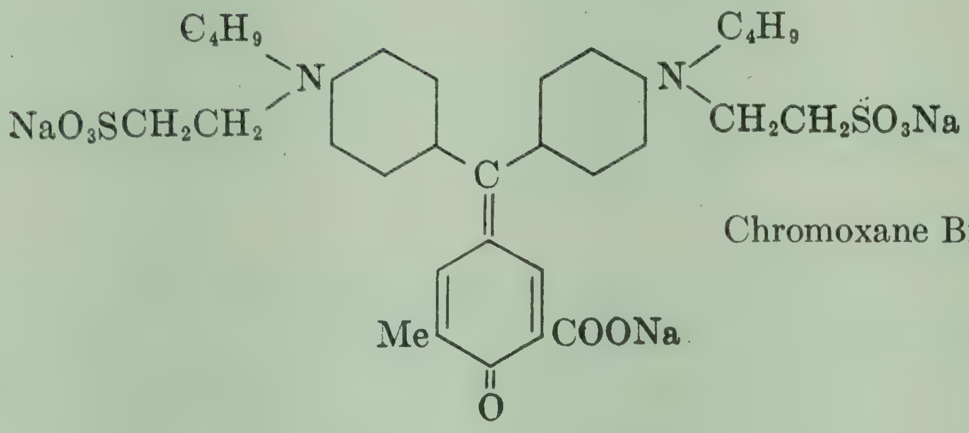
condensed with R-salt, and the leuco compound oxidized to the dye; sulfuric acid is used for the two condensations and the two oxidations are effected by the addition of sodium nitrite; the series of reactions are carried out successively without isolation of the intermediate products. Carrying out the same series of reactions, but using 1-phenyl-3-methyl-5-pyrazolone in place of R-salt, the product is Chromoxane Brown 5R.[10]

In Chromoxane Brilliant Violet 5R, Chromoxane Brilliant Violet BR and Metachrome Violet 2R, there is only one cresotinic acid residue.[10] The first is prepared by condensing 5-aldehydocresotinic acid with *o*-tolyltaurine; the dyestuff is marketed and applied to the fiber as the leuco base and developed by chroming. Chromoxane Brilliant Violet BR has been stated to be specially useful for dyeing blankets and bathing costumes because of its good fastness to stoving and to sea water. Meta-



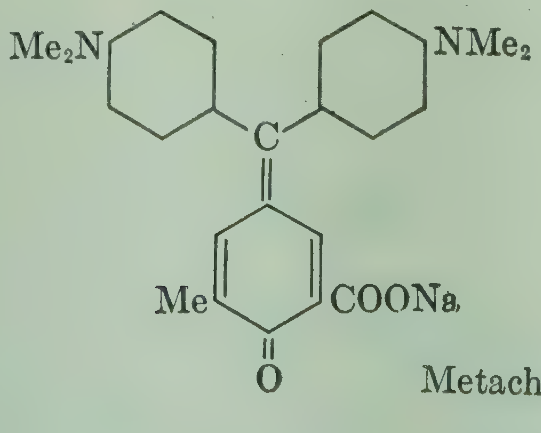
Me
Me
NaO₃SCH₂CH₂HN
NHCH₂CH₂SO₃Na
C
Me
COONa
O

Chromoxane Brilliant Violet 5R



C₄H₉
N
NaO₃SCH₂CH₂
C₄H₉
N
CH₂CH₂SO₃Na
C
Me
COONa
O

Chromoxane Brilliant Violet BR



Me₂N
NMe₂
C
Me
COONa
O

Metachrome Violet 2R

chrome Violet 2R,[10] which is also used as the leuco base, is prepared by the interaction of dimethylaniline, *p*-nitrosodimethylaniline hydrochloride and formaldehyde, the product then being condensed with *o*-cresotinic acid in presence of sulfuric acid. The light fastness of these dyes is 3–4 and the milling fastness is 4.

When salicylic acid residues are used in place of cresotinic acid in dyes of this series, the change in shade on chroming is much less.[51] By condensing 4′-chloro-3-hydroxy-4-carboxybenzophenone with an α-arylindole, and replacing the chlorine atom by a primary or secondary arylamine, dyes giving green shades on chroming are obtained.[52] A method of synthesizing afterchrome dyes starts with the new intermediate 4-hydroxy-5-carboxybenzaldehyde-2-sulfonic acid, which is condensed with two moles of a secondary or tertiary aromatic amine; the resulting triarylmethanes are oxidized to dyes, which give green shades on wool or silk, turned bluer by afterchroming.[53] Dyes have been prepared from *p*-chlorobenzaldehyde and two moles of *m*-cresotinic acid; the halogen is replaced by an arylamine residue, and the products dye wool, afterchromed, in vivid blue shades.[54] The use of hydroxynaphthoic acid derivatives (e.g., 7-sulfo-1-hydroxy-2-naphthoic acid) has been suggested.[55] A mordant dye not containing an *o*-hydroxycarboxylic acid group is prepared by condensing protocatechuic aldehyde with two moles of β-sulfoethyl-*o*-toluidine; the dye may be used as the chromium complex.[55] Triarylmethane dyes derived from 8-hydroxyquinoline have been claimed; for example, the leuco compound obtained by condensing two moles of 8-hydroxyquinoline with one of 4-dimethylamino-2-sulfobenzaldehyde gives, after chroming, a green dye of good washing and fulling fastness on wool.[56] A method for improving solubility in water of chromium compounds of triarylmethane dyes is treatment with a strong acid in an organic solvent.[57] Violet-blue triarylmethane dyes, useful for the preparation of lake pigments, are obtained by the oxidation of a mixture of *o*-phenyl-*N*,*N*-dimethylaniline (*o*-dimethylaminodiphenyl) and phenol.[57a] Derivatives of fuchsone containing hydroxy and alkoxy groups (e.g., compounds obtained by condensing vanillin with 2 moles of guaiacol and oxidizing) have chemotherapeutic properties; some are said to be effective against certain forms of tuberculosis.[58]

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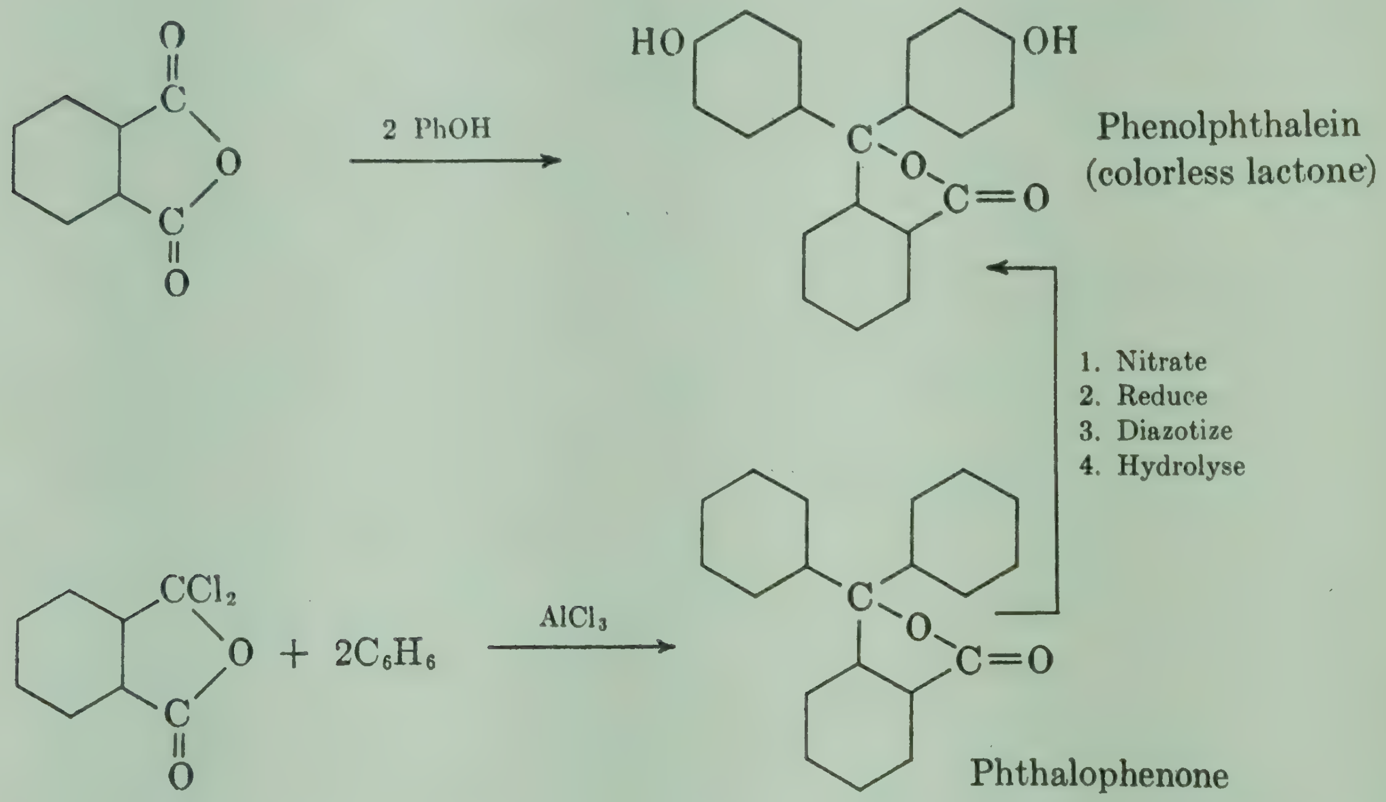
[51] IG, BP 514,450.
[52] IG, BP 514,531.
[53] IG, BP 505,560.
[54] IG, BP 497,030.
[55] IG, BP 471,686.
[56] GP Anm. I. 50,423.
[57] Geigy, BP 497,514.
[57a] General Printing Ink Corp., BP 614,391.

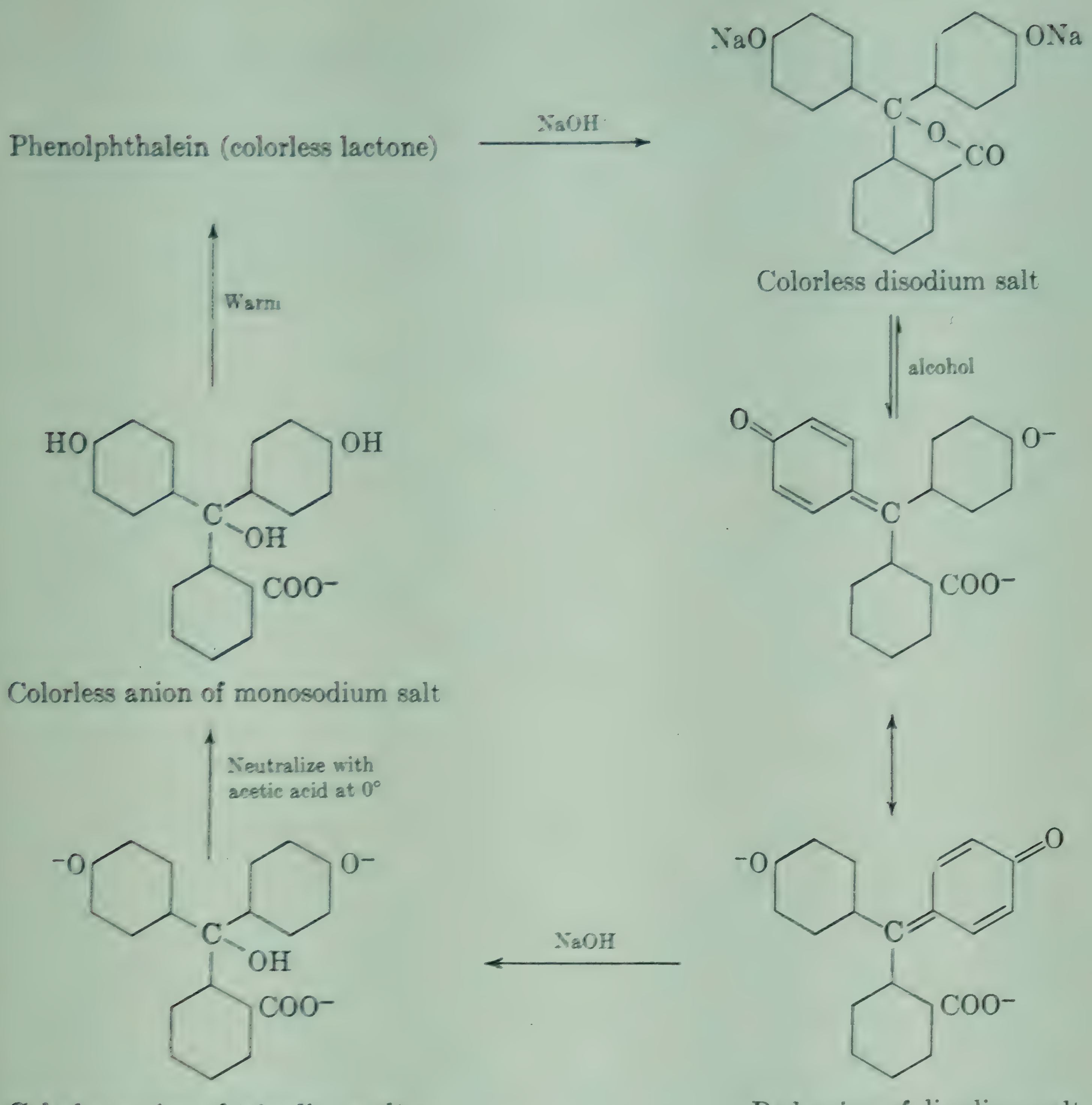
Phthaleins

The indicator Phenolphthalein (BASF, 1871; CI 764), prepared by heating phenol with phthalic anhydride in presence of sulfuric acid or zinc chloride, is a triphenylmethane derivative. It is also structurally related to Fluorescein and other phthaleins; a by-product in the phenolphthalein melt is fluorane, the parent substance of the Fluoresceins and Rhodamines (see Chapter XXIV). Baeyer demonstrated the constitution of phenolphthalein and its relation to triphenylmethane by synthesizing both triphenylmethane and phenolphthalein from phthalic anhydride, *via as*-phthalyl chloride and phthalophenone.[59] The *p*-positions of the two hydroxyl groups were proved by conversion into *p,p'*-dihydroxybenzophenone. When alkali is added to the colorless alcoholic solution of phenolphthalein, an intense red color appears at pH 8.4, and the color is destroyed when excess of alkali is added, as well as by the addition of a large excess of alcohol. The resonance of the ion of the disodium salt and the absence of this optically important resonance in the nonionizing



[58] Chinoin Gyógyszer és Vegyészeti Termékek Gyara R.T., BP 485,228; 485,266; 502,216.

[59] Baeyer, *Ann.* **202,** 36 (1880).

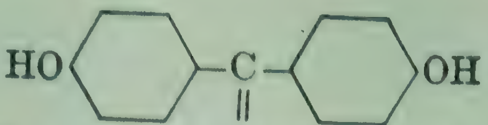

Phenolphthalein (colorless lactone)
NaOH
Colorless disodium salt
alcohol
Warm
Colorless anion of monosodium salt
Neutralize with acetic acid at 0°
NaOH
Colorless anion of trisodium salt
Red anion of disodium salt

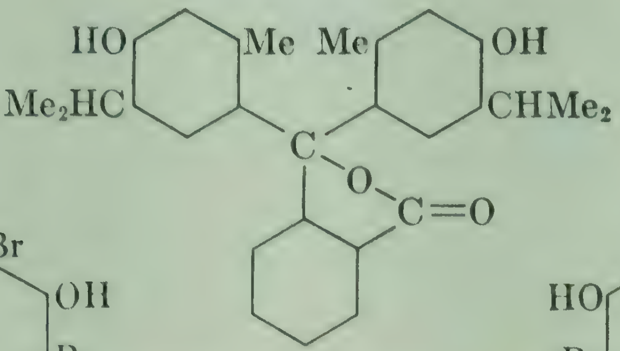
alcoholic solution of the disodium salt and in the ions of the trisodium and monosodium salts explain the indicated decolorizations.[60]

Phenolphthalein is a mild tasteless purgative, which is widely used as an ingredient in laxative preparations. A yellow variety of phenolphthalein, prepared by the zinc chloride method at a slightly higher temperature with formation of tar, has better laxative action; the reason is unknown, but it has been shown that yellow phenolphthalein does not contain α- or β-hydroxyanthraquinone, both of which incidentally are much less potent laxatives than phenolphthalein.[61] The cathartic action

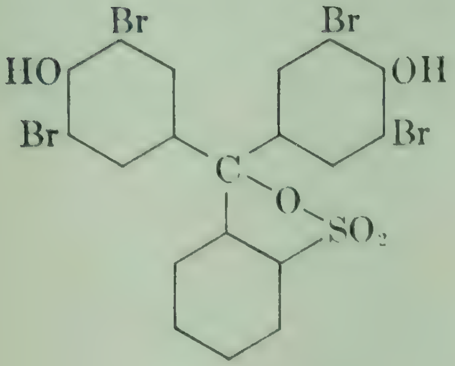
[60] The polarographic behavior of phenolphthalein has been studied by Kolthoff and Lehmicke, *JACS* **70**, 1879 (1948).

[61] Hubacher, USP 1,940,495; 2,192,485; Hubacher and Doenberg, *J. Am. Pharm. Assoc.* **37**, 261 (1948).

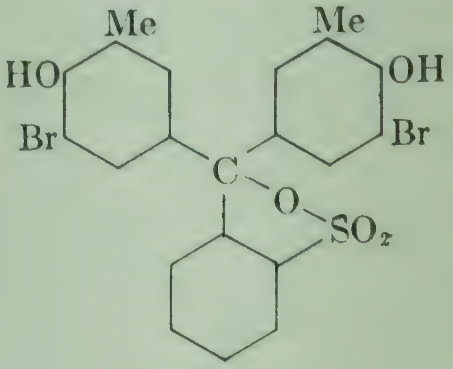
has been ascribed to the  skeleton, and other compounds of the type (e.g., Isacen, the diacetate of the condensation product of phenol and isatin) have been prepared.[62] The disodium salts of tetraiodophenolphthalein and of phenoltetraiodophthalein are used for X-ray examination of the gall bladder; disodium phenoltetrabromophthalein disulfonate is used for testing if the liver is functioning normally.



Thymolphthalein



Bromophenol Blue



Bromocresol Purple

Besides phenolphthalein, cresolphthalein (from *o*-cresol), thymolphthalein and their analogs have been used as indicators. Thymolphthalein changes from colorless to blue at pH 9.3–10.5. The sulfonphthaleins, prepared by condensing phenols with *o*-sulfobenzoic anhydride in presence of zinc chloride, are useful indicators for a wide range of pH.[63] In Table I, a series of sulfonphthaleins are listed, together with the pH at which change of color occurs.[63]

The rate of excretion of Phenol Red has been used for determining if the kidney is functioning normally.

LAKES OF BASIC AND ACID DYES OF THE TRIPHENYLMETHANE, XANTHENE AND SIMILAR SERIES

Basic and acid triarylmethane dyes have been used in lake making for their brightness, but the tannin-antimony lakes of the basic dyes on alumina and the barium lakes of the acid dyes have poor light fastness. The important discovery was made by BASF in 1913 that the phosphotungstic and phosphomolybdic acid lakes have good light fastness, while

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[62] Pyman *et al.*, *Quart. J. Pharm. Pharmacol.* **7**, 509 (1934); Hubacher, *JACS* **64**, 2538 (1942).

[63] Clarke and Lubs, *JACS* **40**, 1443 (1918). A quantitative examination of the stability of the sulfonphthaleins to alkali has been made by Sager, Maryott and Schooley, *JACS* **70**, 732 (1948).

TABLE I
SULFONPHTHALEINS

Indicator	*-sulfonphthalein*	*pH range*	*Color change*
m-Cresol Purple	*m*-Cresol	0.5–2.5 7.6–9.2	Red-Yellow Yellow-Purple
Thymol Blue	Thymol	1.2–2.8 8.0–9.6	Red-Yellow Yellow-Blue
Xylenol Blue	*p*-Xylenol	1.2–2.8 8.0–9.6	Red-Yellow Yellow-Blue
Bromophenol Blue	Tetrabromophenol	3.0–4.6	Yellow-Blue
Bromochlorophenol Blue	Dichlorodibromophenol	3.2–4.8	Yellow-Blue
Bromocresol Green	Tetrabromo-*m*-cresol	3.8–5.4	Yellow-Blue
Chlorophenol Red	Dichlorophenol	4.8–6.4	Yellow-Red
Bromocresol Purple	Dibromo-*o*-cresol	5.2–6.8	Yellow-Purple
Bromophenol Red	Dibromophenol	5.2–6.8	Yellow-Red
Bromothymol Blue	Dibromothymol	6.0–7.6	Yellow-Blue
Phenol Red	Phenol	6.8–8.4	Yellow-Red
Cresol Red	*o*-Cresol	7.2–8.8	Yellow-Red

TABLE II

Fanal color	*Basic dye*
Blue B	Victoria Pure Blue BO
Bremen Blue	Special Blue G (Vulcan Bremen Blue N)
Yellow G	Auramine G
Yellow Green G	Auramine G (63.4%); Green GX (37.6%)
Yellow Green GG	Auramine G (81%); Diamond Green GX (19%)
Pink	Rhodamine 4GD extra
Red 3B	Rhodamine 4GD extra (40.2%); Rhodamine B extra (59.8%)
Red 6B	Rhodamine 3B extra
Violet R	Methyl Violet B extra highly conc.

the phosphomolybdenumtungstate lakes (Immerheiser and Zschimmer, 1923) are still faster and are very brilliant. The Fanal colors (IG) are such lakes of basic and acid triphenylmethane colors, and of basic and derived acid colors belonging to the diphenylmethane, xanthene and similar classes. Several series of Fanal colors are made; these are listed in Tables II–IV; the first column gives the name of the Fanal color and the second the name of the basic dye which is laked.[9, 10, 64]

(1) **The "old series."** Basic dyes are laked in presence of aluminum hydroxide with a complex acid prepared by adding hydrochloric acid to

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[64] *BIOS* 1661.

a solution of the sodium salts of phosphoric, molybdic and tungstic acids. For the preparation of the powder brands the reaction mixture is treated with Emulphor FM to render the lakes dispersible in oils;[65] this also applies to the other series of Fanal colors.

(2) **Extra series.** The basic dyes listed below are laked with a solution obtained by acidifying a solution of sodium molybdate and disodium hydrogen phosphate and reducing with zinc dust.

TABLE III

Fanal color	*Basic dye*
Blue B extra	Victoria Pure Blue BO
Yellow Green G extra	Basic Yellow 52115 (46.5%); Diamond Green GX (53.5%)
Green G extra	Diamond Green GX
Red 6B extra	Rhodamine 3B extra (84.5%); Rhodamine 4GD (15.5%)
Violet R extra	Methyl Violet N Blue

(3) **Supra series.** The basic dye is precipitated by a solution obtained by acidification and zinc dust reduction of a solution of the sodium salts of phosphoric, molybdic, and tungstic acids; in some cases the zinc reduction is omitted.

TABLE IV

Fanal color	*Basic dye*
Blue B Supra	Victoria Pure Blue BO
Blue 3B Supra	Ceres Blue I
Bremen Blue B Supra	Rhoduline Blue 5B
Bremen Blue G Supra	Rhoduline Blue 5B (62%); Diamond Green GX (38%)
Yellow G Supra	Thioflavine TCN
Yellow Green G Supra	Basic Yellow 52115 (40%); Diamond Green GX (60%)
Green G Supra	Diamond Green GX
Pink B Supra	Rhodamine 4GD extra
Pink G Supra	Rhodamine 5GD extra (93%); Auramine 0 (7%)
Red B Supra	Astraphloxine FF extra
Red 6B Supra	Rhodamine 3B extra (84.6%); Rhodamine 5GD extra (15.4%)
Violet R Supra	Methyl Violet N Blue
Violet 3R Supra	Red Violet for Fanal dye

(4) **M-series.** A solution of potassium ferrocyanide and sodium sulfite is added to a solution of the basic dye and copper sulfate at about 70°.

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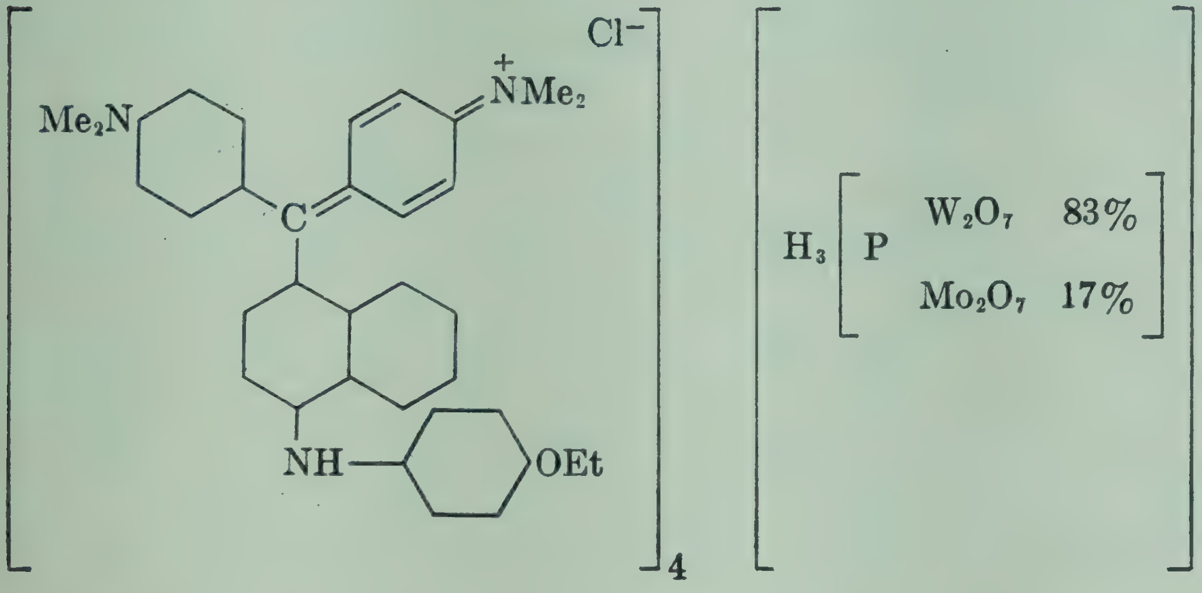
[65] Emulphor FM is triethanolamine monooleate; see also *BIOS* **421.**

TABLE V

Fanal dye	*Basic dye*
Blue RM	Ethyl Violet BNOO
Pink BM	Rhodamine 4GD extra
Red 6BM	Rhodamine 3B extra (89%); Rhodamine 4GD extra (11%)
Violet RM	Methyl Violet N Blue
Violet 3RM	Trioxybutylfuchsine

The constitution of the Fanal colors is uncertain. For Fanal Blue 3B Supra the probable composition has been stated; the lake is made from Ceres Blue I, the basic dye obtained from Michler's ketone and *p*-ethoxyphenyl-α-naphthylamine.

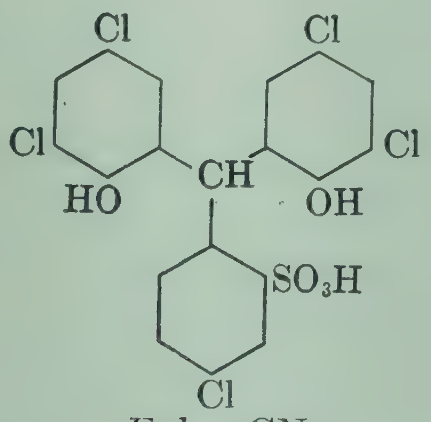


Fanal Blue 3B

Fanal L brand lakes are made by dry grinding a mixture of an acid dyestuff, Fanal Salt WM [$P(W_2O_7)_6Na_3H_4$, $16H_2O$], rock salt and dextrin.[64]

Moth-Proofing Agents

Colorless triphenylmethane derivatives have been used as moth-proofing agents. An example is Eulan CN (IG) (Lanoc CN).[66]



Eulan CN

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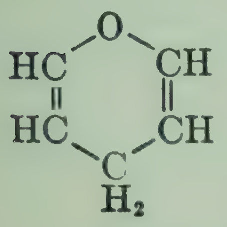
[66] For an account of the manufacture and properties of IG products for pest control, see *BIOS* **1480.**

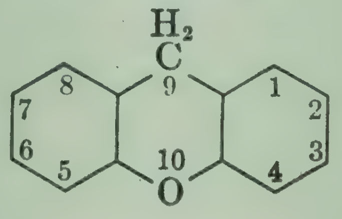
Chapter XXIV

XANTHENE AND ACRIDINE DYES

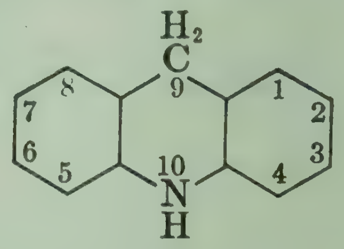
The heterocyclic ring system, xanthene or dibenzo-γ-pyran, is the inner anhydride of *o,o′*-dihydroxydiphenylmethane and the oxygen analog of 9,10-dihydroacridine. γ-Pyran itself has not yet been synthesized, but xanthene has been obtained by the distillation of *o,o′*-dihydroxydiphenylmethane, as a decomposition product of aluminum phenoxide, and by the distillation of xanthone with zinc dust. Xanthone can be prepared in several ways, e.g., by heating salicylic acid with acetic anhydride; and some naturally occurring yellow coloring matters are xanthone derivatives.[1] Euxanthone, found in the urine of cows fed on mango leaves, is 1,7-dihydroxyxanthone, and gentisin, the coloring matter of gentian root, is 1,7-dihydroxy-3-methoxyxanthone.



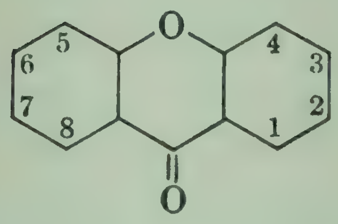
γ-Pyran



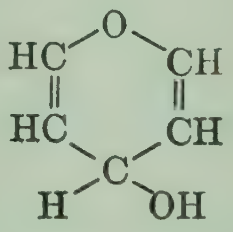
Xanthene



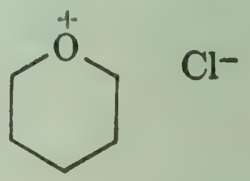
9,10-Dihydroacridine



Xanthone



γ-Pyranol



Pyrylium chloride

Derivatives of 2- and 3-phenylbenzo-γ-pyrones (flavones and isoflavones) are widespread in nature; an example is quercetin (3,5,7,3′,4′-pentahydroxyflavone), which occurs in numerous plants. Extracts of the bark of the oak *Quercus tinctoria* which contains quercitrin (quercetin 3-rhamnoside), old fustic which contains morin (3,5,7,2′,4′-pentahydroxyflavone) and maclurin (2,4,6,3′,4′-pentahydroxybenzophenone), and Persian berries which contain rhamnetin and rhamnazin (7-methyl and 7,3′-dimethyl ethers of quercetin) are among the natural coloring matters of the flavone group which were largely used at one time as mordant

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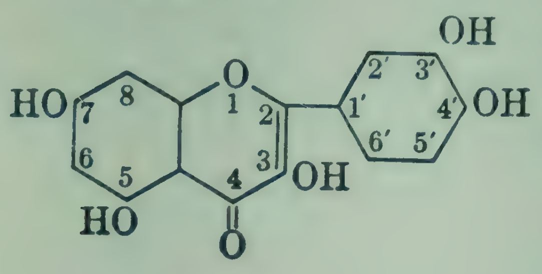
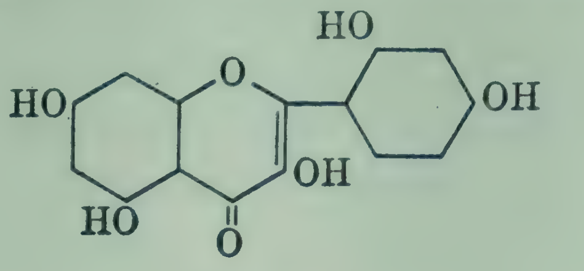
[1] For refs., see Mayer translated by Cook, The Chemistry of Natural Organic Coloring Matters, Reinhold, New York, 1943. See also Perkin and Everest, The Natural Organic Coloring Matters, Longmans, London, 1918.



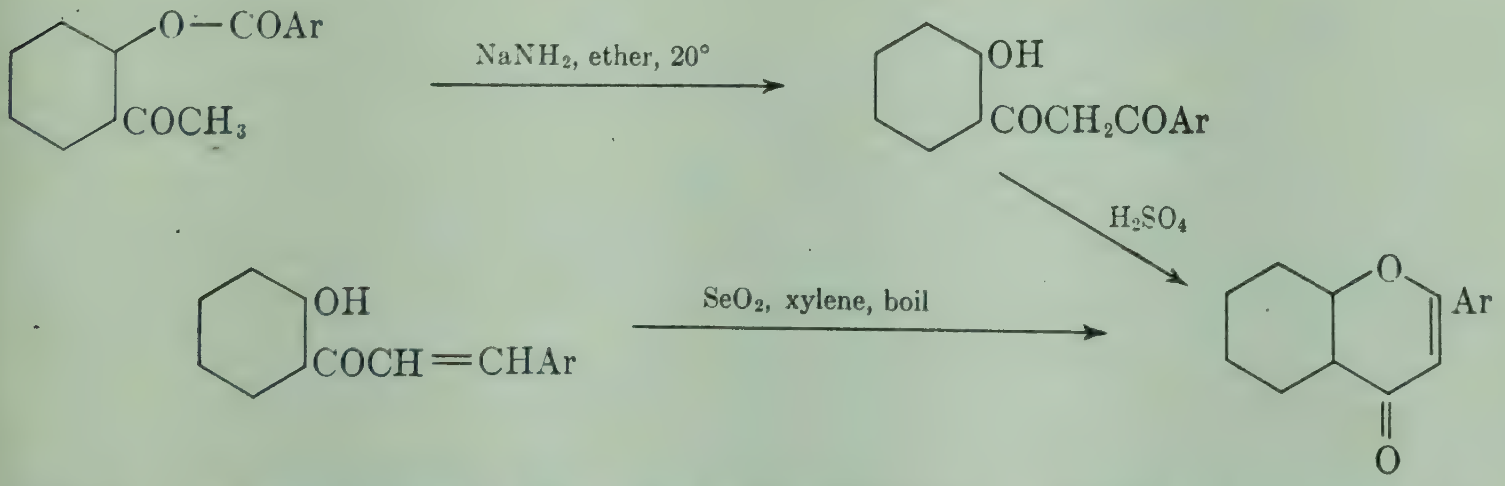
Quercetin



Morin

dyes for yellow, orange and olive shades, especially in calico printing.[1] These natural coloring matters, especially fustic, are still used to a limited extent. 3-Hydroxyflavones (flavonols) are distinct in some of their properties from flavones not containing a hydroxyl group in the 3-position; as mordant dyes the former give deeper shades than the corresponding flavones; flavonols in aqueous alkaline solution are rapidly decomposed by atmospheric oxygen.

A general method for the synthesis of flavones and flavonols is the Robinson reaction[1] in which an *o*-hydroxyacetophenone, such as phloracetophenone or ω-methoxyphloracetophenone, is heated with the anhydride and the sodium salt of benzoic or a substituted benzoic acid; after hydrolysis of *O*-benzoyl groups (as well as a *C*-benzoyl group which sometimes enters the 3-position) and demethylation, if necessary, the flavone or flavonol is obtained. The Robinson reaction involves the transformation of an *o*-benzoyloxyacetophenone to an *o*-hydroxydibenzoylmethane and subsequent cyclization to a flavone; the diketone can be isolated in good yield by treating the *o*-benzoyloxyacetophenone with a base such as potassium carbonate, sodamide or caustic potash in toluene, ether, or pyridine.[2] A method for the synthesis in high yield of flavones unsubstituted in the 3-position is the action of selenium dioxide on an *o*-hydroxychalkone.[1] The Elbs persulfate oxidation of a phenol to a hydroquinone has been found to be of great value for the synthesis of polyhydroxyflavones and -flavonols.[3]

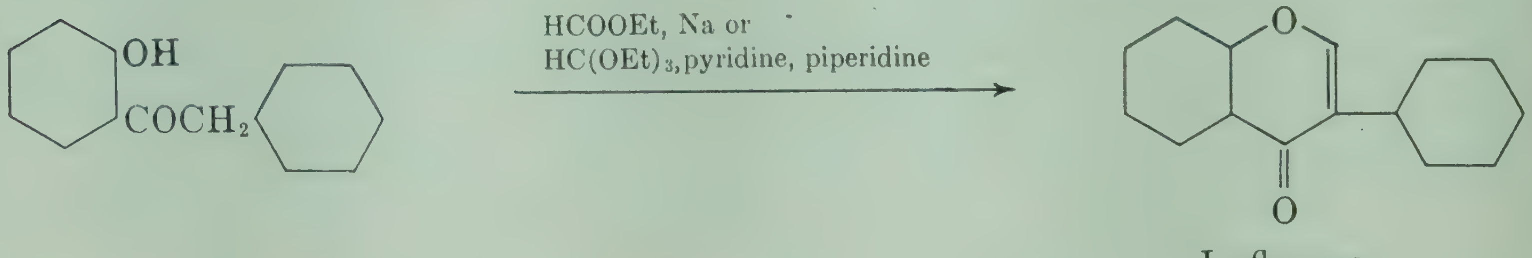


[2] Baker, *JCS* 1381 (**1933**); Mahal and Venkataraman, *Current Sci.* (*India*) **2,** 214 (1933); Wheeler *et al.*, *JCS* 340 (**1950**); *et seq.*

[3] Rao and Seshadri, *Proc. Indian Acad. Sci.* **25A,** 417 (1947), *et seq.*

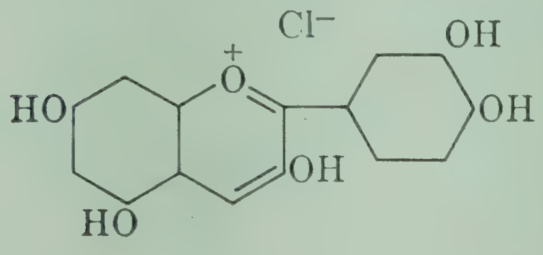
Rutin, the 3-rutinoside of quercetin occurring in various plants, exhibits vitamin P activity or the regulation of capillary fragility and permeability (Szent-Györgyi, 1936); a flavanone or 2,3-dihydroflavone derivative, which has similar activity, is hesperidin, the 7-rutinoside of 5,7,3′-trihydroxy-4′-methoxyflavanone.

A general method for the synthesis of isoflavones, which have feebler tinctorial properties than flavones and flavonols, is the interaction of an *o*-hydroxyphenyl benzyl ketone with ethyl formate and sodium, or with ethyl orthoformate, pyridine and piperidine.[1, 4] Examples of naturally occurring isoflavones are prunetin (5,4′-dihydroxy-7-methoxyisoflavone) and santal which contains an additional hydroxyl group in the 3′-position.

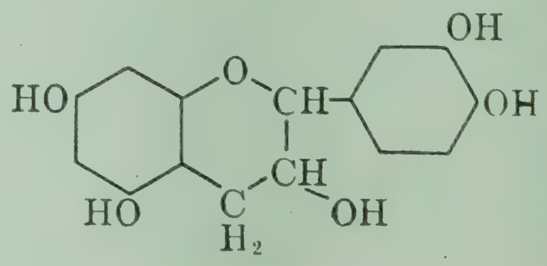


Isoflavone

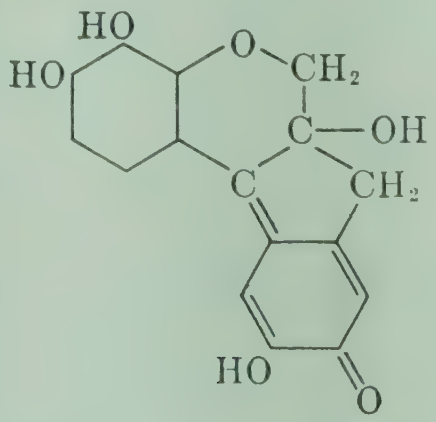
The γ-pyran ring in the form of pyrylium salts (oxonium salts of the carbinol base, γ-pyranol) occurs in the anthocyanins, the red, violet and blue coloring matters of flowers and fruits. An example is cyanidin chloride; the 3,5-diglucoside, cyanin, is the coloring matter of the red rose and the cornflower. The anthocyanins (and the aglycones, anthocyanidins) have mordant dyeing properties, but are quite valueless as dyes since they are unstable to water and alkali; they undergo characteristic color changes, useful for identification when the pH of an aqueous



Cyanidin chloride



Catechin



Haematein

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[4] Sathe and Venkataraman, *Current Sci.* (*India*) **18,** 373 (1949); Iyer, Shah, and Venkataraman, *ibid.* 404.

solution is progressively altered (G. M. and R. Robinson).[1] γ-Pyrones are reduced to γ-pyranols by lithium aluminum hydride, and acid treatment then gives pyrylium salts; thus quercetin can be converted to cyanidin chloride.[4a] A widely applicable reaction (Robinson) for the synthesis of anthocyanidins and anthocyanins is the condensation of a salicylaldehyde and an ω-hydroxyacetophenone in presence of hydrogen chloride.[1]

Catechin is a constituent of the red heartwood of *Acacia catechu*, the fruit of *Areca catechu*, the leaves and twigs of *Uncaria gambier*, and several other plants. It is a colorless water-soluble substance which dyes brown shades ("cutch or catechu brown") in conjunction with copper sulfate and sodium dichromate. Catechu or cutch, the dried aqueous extract used for dyeing and also for tanning, contains "catechutannic acid" besides catechin. Cutch brown was reputed at one time to be very fast to light, acid and alkali. While this is not true according to modern standards, it still remains a useful shade and continues to be used for dyeing awnings, sail-cloth, fishing nets, and other cotton materials on which cutch brown exercises a preservative action; cutch is also used for dyeing wool and silk and for weighting the latter. Catechin is 3,5,7,3′,4′-pentahydroxyflavan, and contains two asymmetric carbon atoms; several stereoisomeric catechins occur in nature. Cyanidin chloride can be reduced to *dl*-epicatechin, and the reverse conversion of *d*-catechin to cyanidin has been effected by a series of reactions. The catechin skeleton is perhaps the precursor of the phloroglucinol tannins. A tannin red or phlobaphen is produced by heating an aqueous solution of cutch with a mineral acid. Catechin has been found to exhibit high vitamin P activity (Lavollay, 1943).

Logwood extract (from the wood of *Haematoxylon campechianum*) is a natural coloring matter which is still used extensively for dyeing silk, wool and linen, and to a minor extent for calico printing. It yields rich deep blacks with iron and copper mordants. Silk dyed logwood black acquires a characteristic finish as a result of the swelling and weighting of the fiber produced by the somewhat complicated mordant-dyeing process which is customarily employed. The red coloring matter, haematein, occurs in logwood as the colorless dihydro derivative, haematoxylin.[1] The analogous brazilein and brazilin of brazilwood (one of the "soluble redwoods") are devoid of the hydroxyl group in the 8-position.[1]

XANTHENE DYES

The first synthetic xanthene coloring matters were the phthaleins (By, 1871), such as Fluorescein, Gallein and Coerulein prepared by con-

[4a] Mirza and Robinson, *Nature* **166**, 997 (1950).

densing phthalic anhydride with resorcinol, pyrogallol or gallic acid. The phthalein dyes became technically important when a method for the manufacture of phthalic anhydride from naphthalene was developed some years later. The Rhodamines and Pyronines, which are derived from *m*-alkylaminophenols and are basic dyes of the xanthene group, were discovered in 1887–91 (Céresole; Kahn and Majert; Bender), and because of the brilliance and beauty of the shades some of the earliest Rhodamines are still among the most important dyes for calico printing in spite of their poor fastness properties.[5]

Classification and general properties. The xanthene dyes may be divided into two main groups: (1) diphenylmethane derivatives, called Pyronines, and (2) triphenylmethane derivatives, which mainly consist of the phthaleins prepared by phthalic anhydride condensations, but which also include a small group (sometimes called Rosamines) of 9-phenylxanthene derivatives prepared from substituted benzaldehydes. The phthaleins may be further divided into (a) Fluoresceins, which contain hydroxyl groups; (b) Rhodamines which contain alkylamino or arylamino groups; and (c) mixed types, which contain both hydroxyl and amino groups.

Structurally the xanthene dyes are resonance hybrids of ammonium, oxonium and carbonium structures, but they are conventionally written as oxonium salts. In their dyeing properties the xanthene dyes resemble the triphenylmethane coloring matters. They are mainly basic dyes, useful for dyeing wool, silk and tannin-mordanted cotton and for calico printing; some members of the series are especially valued for the last purpose, notwithstanding their very poor light fastness. Acid dyes are obtainable by the introduction of sulfonic groups; the Fluoresceins, which contain carboxyl and phenolic hydroxyl groups, are also acid colors useful for silk dyeing. Some of the Fluoresceins, particularly those in which the carboxyl group has been esterified, are soluble in alcohol, and are useful for coloring spirit varnishes. By the introduction of *o*-dihydroxy groups and salicylic acid residues, mordant dyes, some of which are valuable as chrome-dyeing colors for wool and chrome-printing colors for cotton, are produced. The shades available in the xanthene series are restricted to reds, pinks and violets, notable for their brilliance. A characteristic property of most of the xanthene dyes, especially the phthaleins, is their fluorescence, which is usually an unattractive feature and decreases their value in dyeing and printing. The fluorescence of some dyes is observed on wool and silk, but not on tannin-mordanted cotton.

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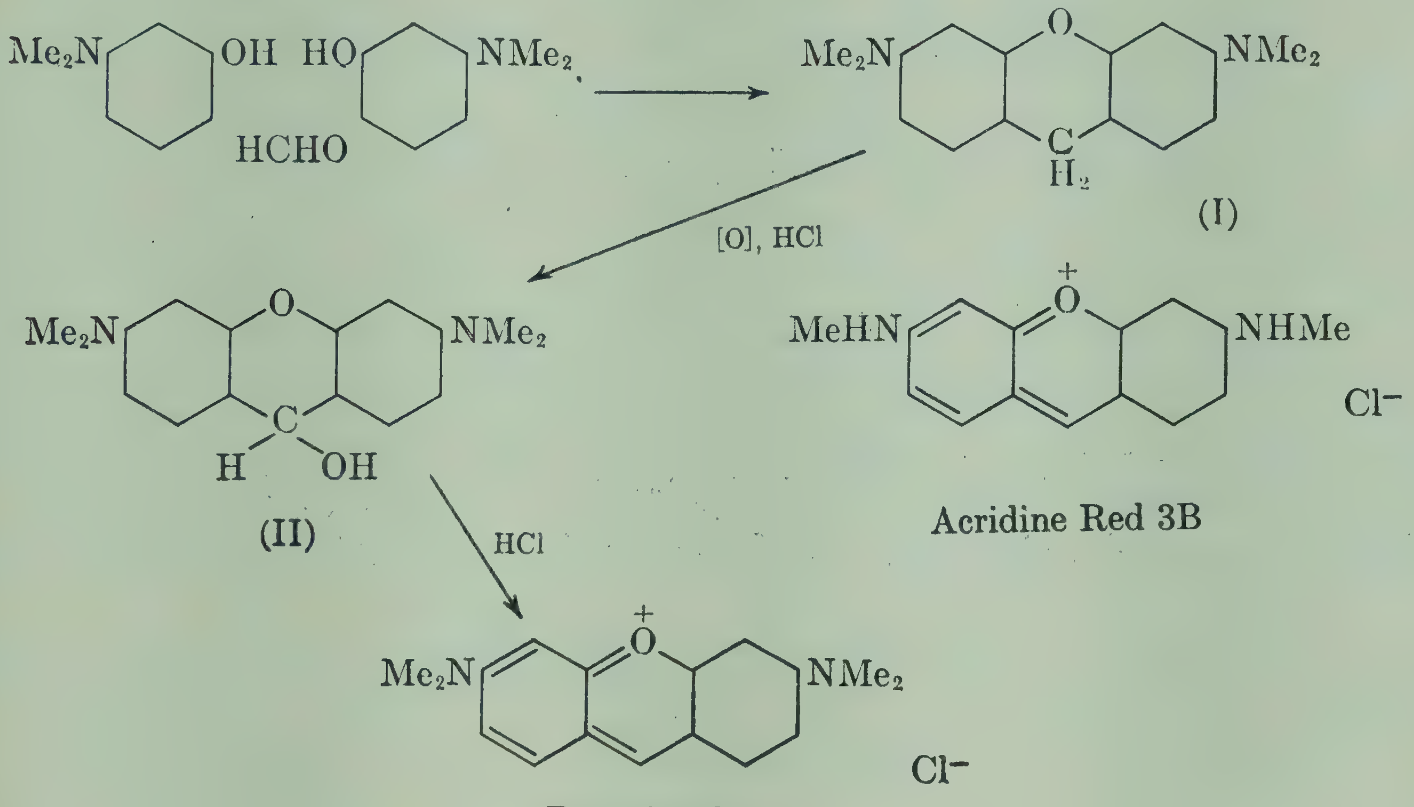
[5] Hewitt, Dyestuffs Derived from Pyridine, Quinoline, Acridine and Xanthene, Longmans, London, 1922; Hewitt in Thorpe's Dictionary of Applied Chemistry, Vol. I, Longmans, London, 1937.

Pyronines. Pyronines are obtained by condensing *m*-dialkylaminophenols with formaldehyde in presence of concentrated sulfuric acid, and oxidizing the xanthene derivative (I) to the xanthhydrol (II) which combines with acid to form the dye. The usual procedure is to treat the xanthene with ferric chloride and nitrous acid in hydrochloric acid solution. Pyronine G (Bender, 1889) (By; CI 739) is a red basic dye which has a yellow fluorescence. When Pyronine is treated with potassium permanganate, two methyl groups are eliminated, and the product is Acridine Red 3B (L; CI 740).



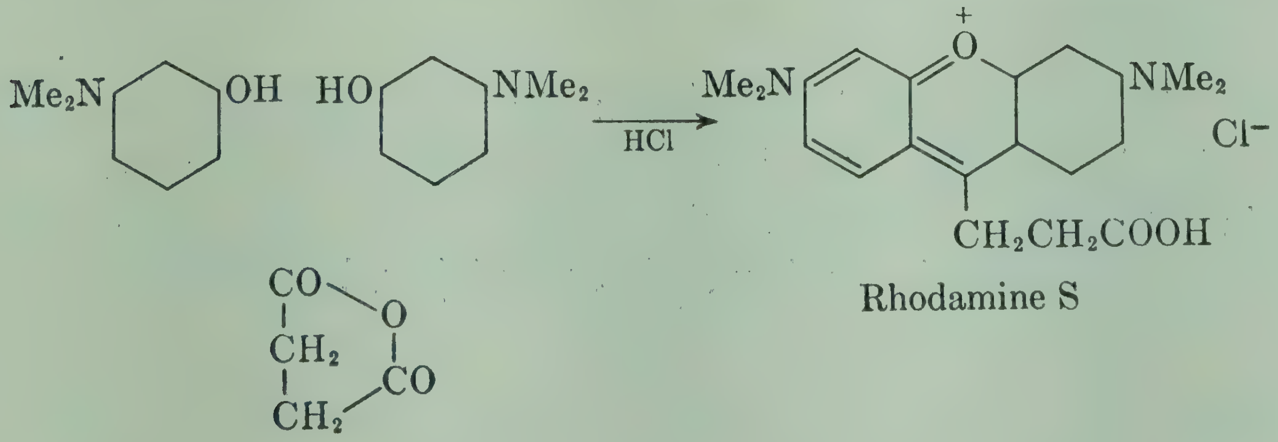
(I)

(II)

Acridine Red 3B

Pyronine G

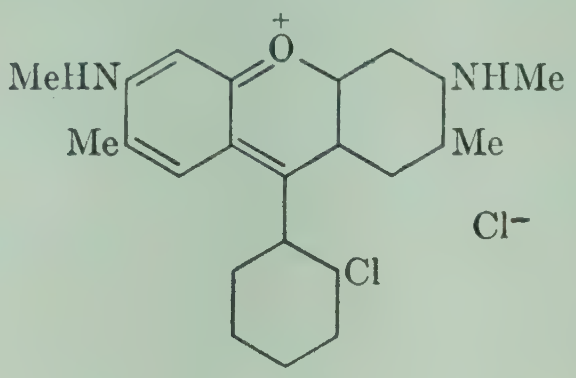
If two moles of a *m*-dialkylaminophenol are condensed with the anhydride of a dicarboxylic acid, such as succinic or phthalic acid, dyes are formed directly; with succinic anhydride the products belong to the Pyronine group, while with phthalic anhydride they are triphenylmethane derivatives. Rhodamine S (Kahn and Majert, 1888) (By; CI 743), the condensation product of *m*-dimethylaminophenol and succinic



Rhodamine S

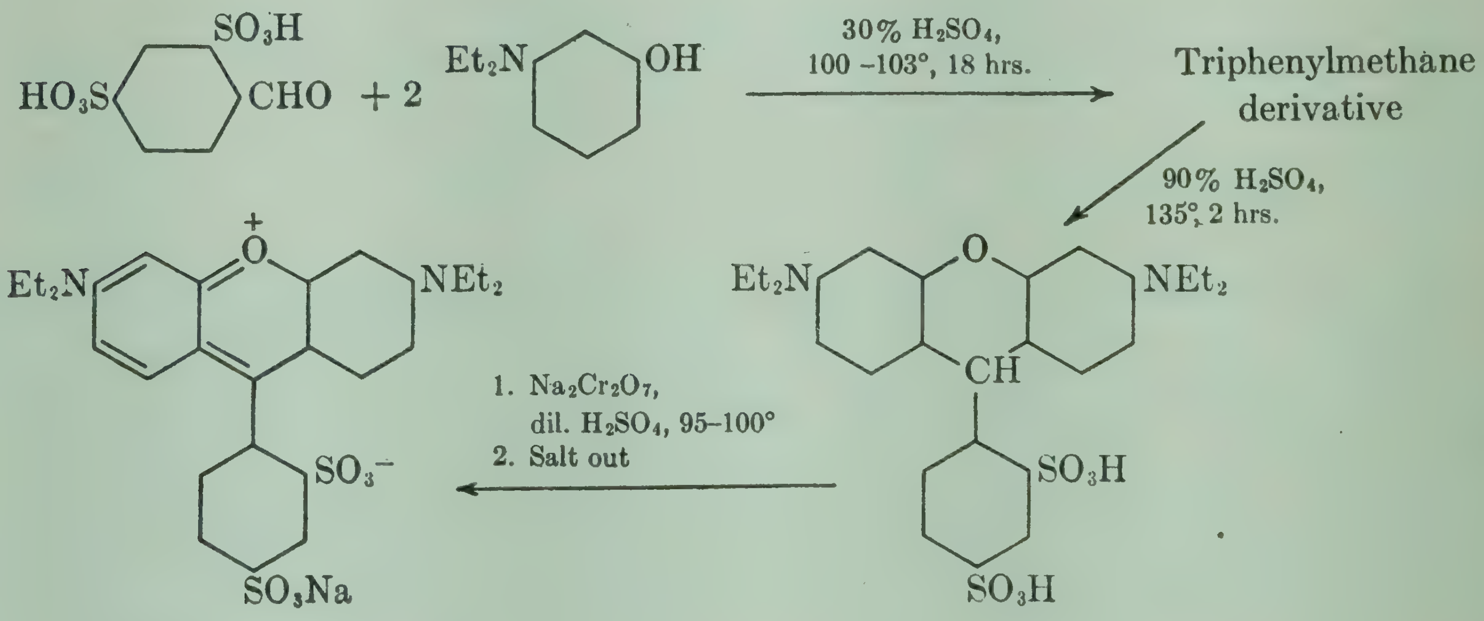
anhydride, has a limited use for pink shades on tannin-mordanted cotton and for coloring paper and wood.

Triphenylmethane derivatives. The replacement of formaldehyde by benzaldehyde in the Pyronine synthesis gives a triphenylmethane or 9-phenylxanthene derivative, which possesses useful properties as a dye if the aromatic aldehyde carries a suitable substituent in the *o*-position. Thus *o*-chlorobenzaldehyde and 2-methylamino-*p*-cresol give Rhodamine 5G (By; CI 746), a brilliant red basic dye with somewhat better fastness properties than Pyronine G.


MeHN
NHMe
Me
Me
Cl⁻
Cl

Rhodamine 5G

Useful acid dyes are obtained by condensing benzaldehyde-2,4-disulfonic acid with *m*-alkylaminophenols. Condensation with *m*-diethylaminophenol (to which is added about 8% of 2-ethylamino-*p*-cresol for shade adjustment) leads to Sulforhodamine B extra (MLB; CI 748), a bright bluish-red acid dye. Sulforhodamine G extra is a similar dye prepared from 2-ethylamino-*p*-cresol; the difference in the method of preparation is that the leuco compound is oxidized to the dye by means of ferric chloride.[6] Sulforhodamine B and G are level-dyeing and have good fastness to alkali, stoving and carbonizing, but poor light fastness (1–2).


SO₃H
HO₃S
CHO + 2
Et₂N
OH
30% H₂SO₄,
100–103°, 18 hrs.
Triphenylmethane derivative
90% H₂SO₄,
135°, 2 hrs.
Et₂N
NEt₂
CH
SO₃H
SO₃H
1. Na₂Cr₂O₇,
dil. H₂SO₄, 95–100°
2. Salt out
Et₂N
NEt₂
SO₃⁻
SO₃Na

Sulforhodamine B extra

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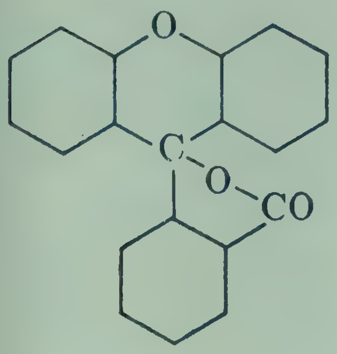
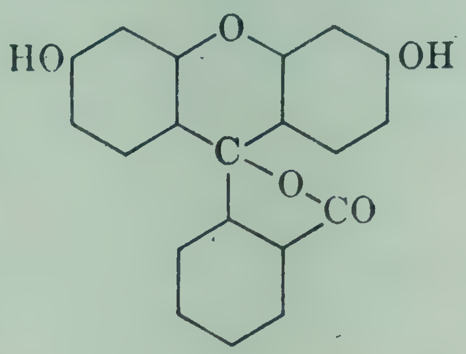
[6] *BIOS* 959.

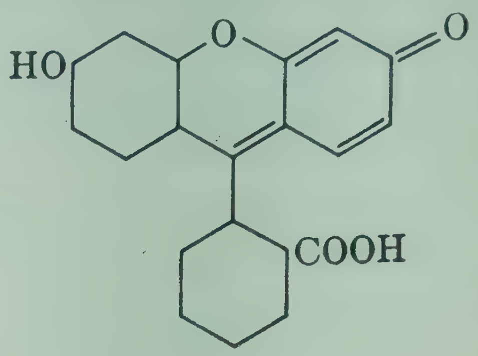
Phthaleins. The parent substance of this group, fluorane, is formed as a by-product in the phenolphthalein melt by part of the phenol condensing in the *o*-position. 2,7-Dimethylfluorane, obtained by the condensation of *p*-cresol with phthalic anhydride in presence of sulfuric acid at 135°, is converted into dimethylceroxonol by treatment with 24% oleum at 10–20°; treatment of the latter with zinc dust, ammonia and caustic soda in an autoclave at 120° for a few hours gives dimethylceroxene, which is sublimed and marketed as Fluorol 5G (IG) for the coloration of motor fuels.[7] The condensation of resorcinol with phthalic anhydride in presence of concentrated sulfuric acid, which is a well known test for resorcinol derivatives as well as the anhydrides of *o*-dicarboxylic acids, gives Fluorescein (By; CI 766). Both the yellow amorphous form and red crystalline form (the latter having a green iridescence) correspond to the more stable quinonoid structure (B); and the compound can also be isolated in the colorless lactone form A (needles from acetic acid). It dissolves in alkali with a red color and a splendid green fluorescence, which is marked even at extremely high dilutions and is therefore useful for such purposes as determining the flow of water. In the form of the sodium or potassium salt, Uranine (CI 766), it is used in dyeing brilliant yellow shades on wool and silk. The principal use of Fluorescein, however, is for halogenation. By treatment of a boiling alcoholic solution with bromine and sodium chlorate, four bromine atoms



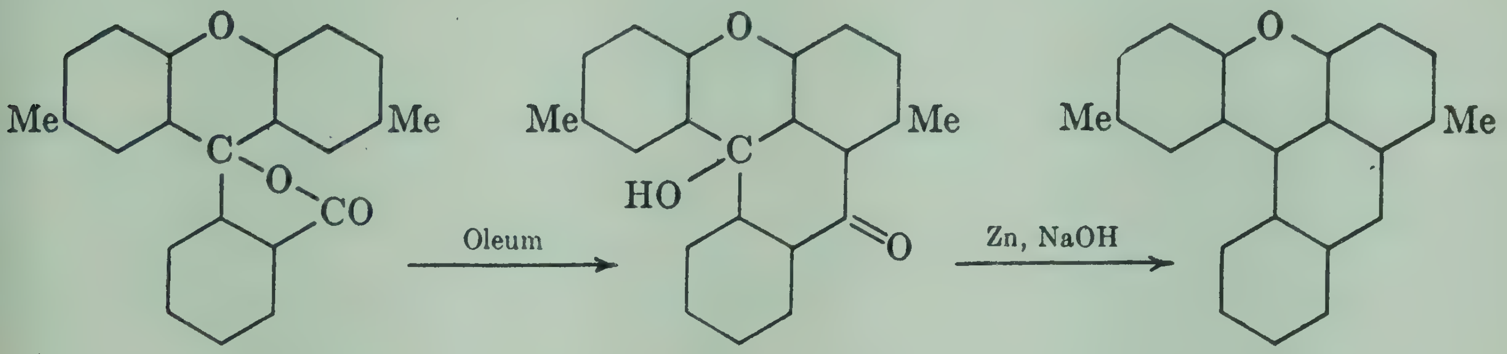
Fluorane



(A)



Fluorescein (B)



2,7-Dimethylfluorane

Dimethylceroxonol

Fluorol 5G

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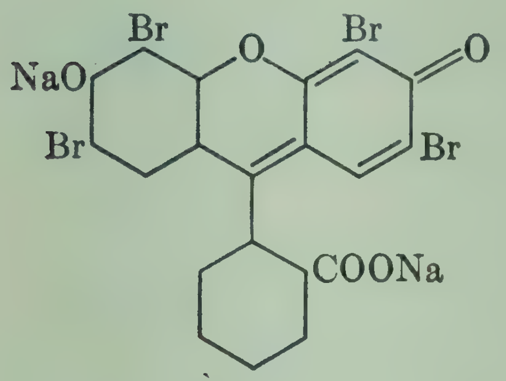
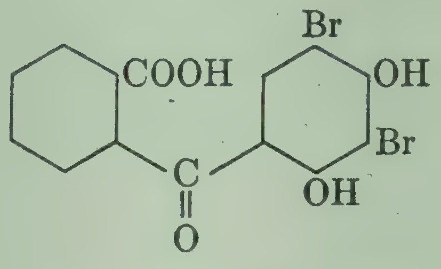
[7] *BIOS* **1433.**

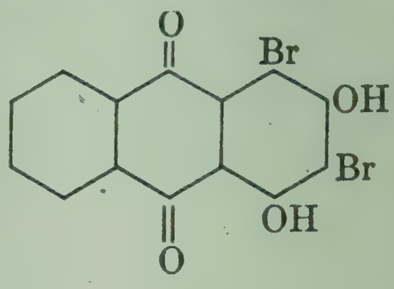
can be introduced, and the product is Eosine (CI 768), which dyes silk red with a brilliant yellow fluorescence; its main use is for coloring inks, and minor uses are for dyeing paper and coloring cosmetics. The orientation of the bromine atoms in Eosine is in accordance with expectation by analogy with the bromination of phenol and resorcinol, and it has been definitely proved by alkali fusion of Eosine to a dibromodihydroxybenzoylbenzoic acid (I), which can be cyclized with sulfuric acid to the known dibromoxanthopurpurin (II); further, by heating (I) above its melting point, Eosine and phthalic acid are obtained (G. Heller; R. Meyer). Using iodine and potassium iodate, the tetraiodo analog, Erythrosine B or J (Kussmaul, 1876; CI 773), is obtained, which dyes a bluer shade than Eosine; it is also useful for coloring food and as an adsorption indicator. Eder observed in 1883 that Erythrosine is a valuable green sensitizer for photographic plates, and it is still used for this purpose. Both Erythrosine B, and the triiodo compound, Erythrosine A, are employed as microscopical stains. Erythrosine 6G (IG) is a mixture of monoiodo- and a little diiodofluorescein.[6] Spirit Eosine (Eosine S) (CI 770), the ethyl ester of Eosine prepared by the usual esterification methods, gives faster and more attractive shades than Eosine, and it is used in coloring spirit varnishes. Dibromofluorescein and dibromodinitrofluorescein (CI 771) have a limited use, and are marketed under the names Eosine H8G (IG) and Eosine BNX (IG).[6] Eosine BNX is prepared by bromination of an aqueous alkaline solution



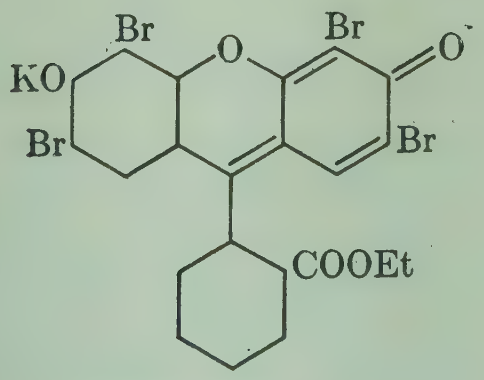
Eosine



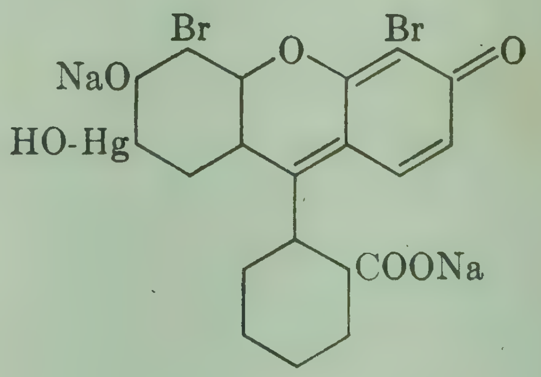
(I)



(II)



Eosine S

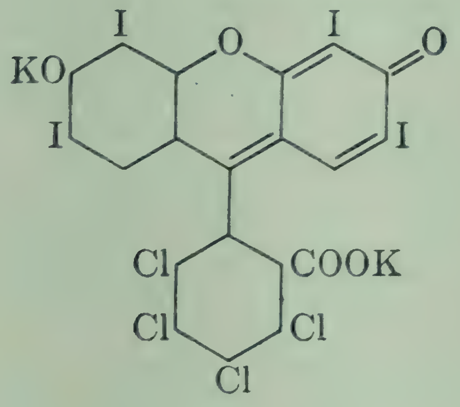


Mercurochrome

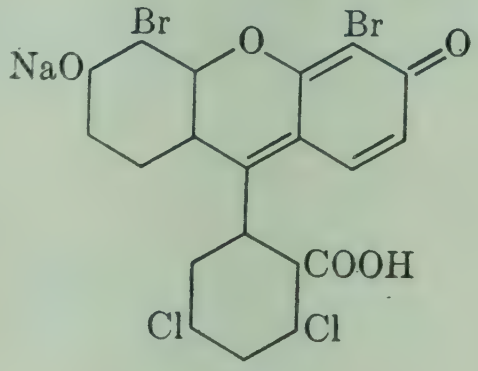
of Fluorescein, followed by treatment with concentrated sulfuric and nitric acids; the product is marketed as the ammonium salt.[6]

Mercurochrome (Merbromin), an important antiseptic, is mercuridibromofluorescein, prepared by brominating Fluorescein in acetic acid solution to the dibromo compound, and heating the latter with mercuric acetate or yellow mercuric oxide in the same solvent. The product is then converted into the disodium salt. The indicated constitution follows from the dibromination of Fluorescein in the 4,5-positions as shown by the formation of 2-bromoresorcinol when dibromofluorescein is fused with alkali.[8] It was the first organic mercurial to be introduced as a general antiseptic (1918), and its value is due to its nonirritant character. It is used extensively for disinfection of the skin, mucous surfaces and wounds, and also administered internally for certain infections.

By using chloro derivatives of phthalic anhydride in the fluorescein reaction, and further brominating or iodinating, a series of related dyes are obtained. Rose Bengal GTO (IG) is a mixture of tri- and tetraiodo derivatives of dichlorofluorescein prepared by condensing resorcinol with 3,5- or 3,6-dichlorophthalic anhydride.[6] The tetraiodo derivative of the fluorescein prepared from di- or tetrachlorophthalic anhydride is Rose Bengal B (Gnehm, 1882) (Cb; CI 779). Dibromination of dichlorofluorescein gives Phloxine N (IG).[6] Other Phloxine brands (CI 778) have been stated to be tetrachlorotetrabromofluorescein.



Rose Bengal B



Phloxine N

Scheckfarbe AS (IG) is a naphthalene analog of Fluorescein, prepared by melting 1,6-dihydroxynaphthalene and phthalic anhydride at 180–200° for two hours;[7] it is used for printing cheques since it is very sensitive to the reagents used for erasure of ink.

Two important mordant dyes are included in this class. By heating a mixture of gallic acid, phthalic anhydride and concentrated sulfuric acid, Gallein (CI 781), which gives a violet shade on chromed wool, is produced. Gallein undergoes dehydration and cyclization on heating with concentrated sulfuric acid, and yields the anthracene derivative, Coerulein (CI 783), which dyes green on chrome mordant. The soluble bisulfite compound of Coerulein, Coerulein S (Prud'homme, 1879), is a valuable chrome-printing color (green and olive shades) for cotton.

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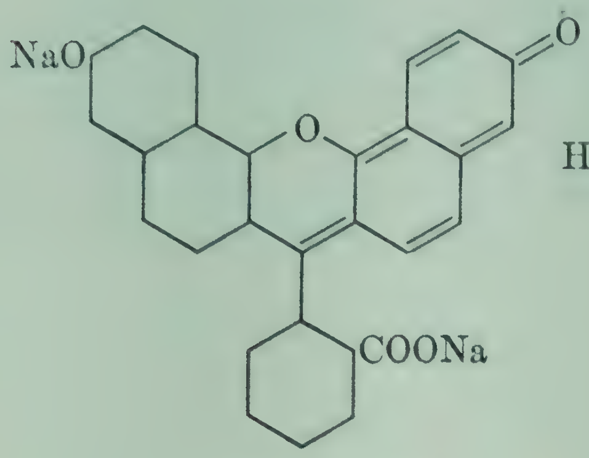
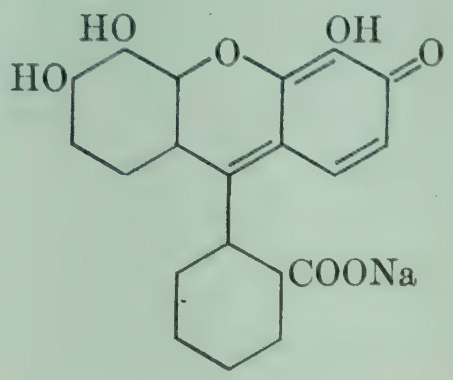
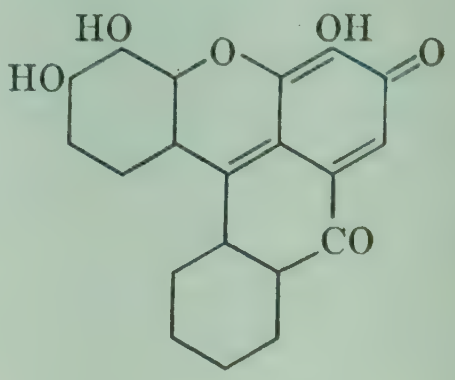
[8] Sandin, Gillies and Lynn, *JACS* **61,** 2919 (1939).



Scheckfarbe AS

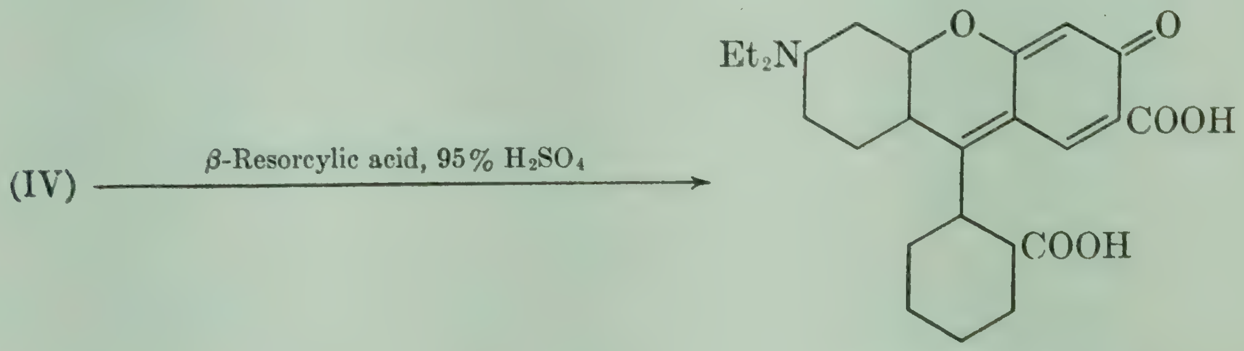


Gallein



Coerulein

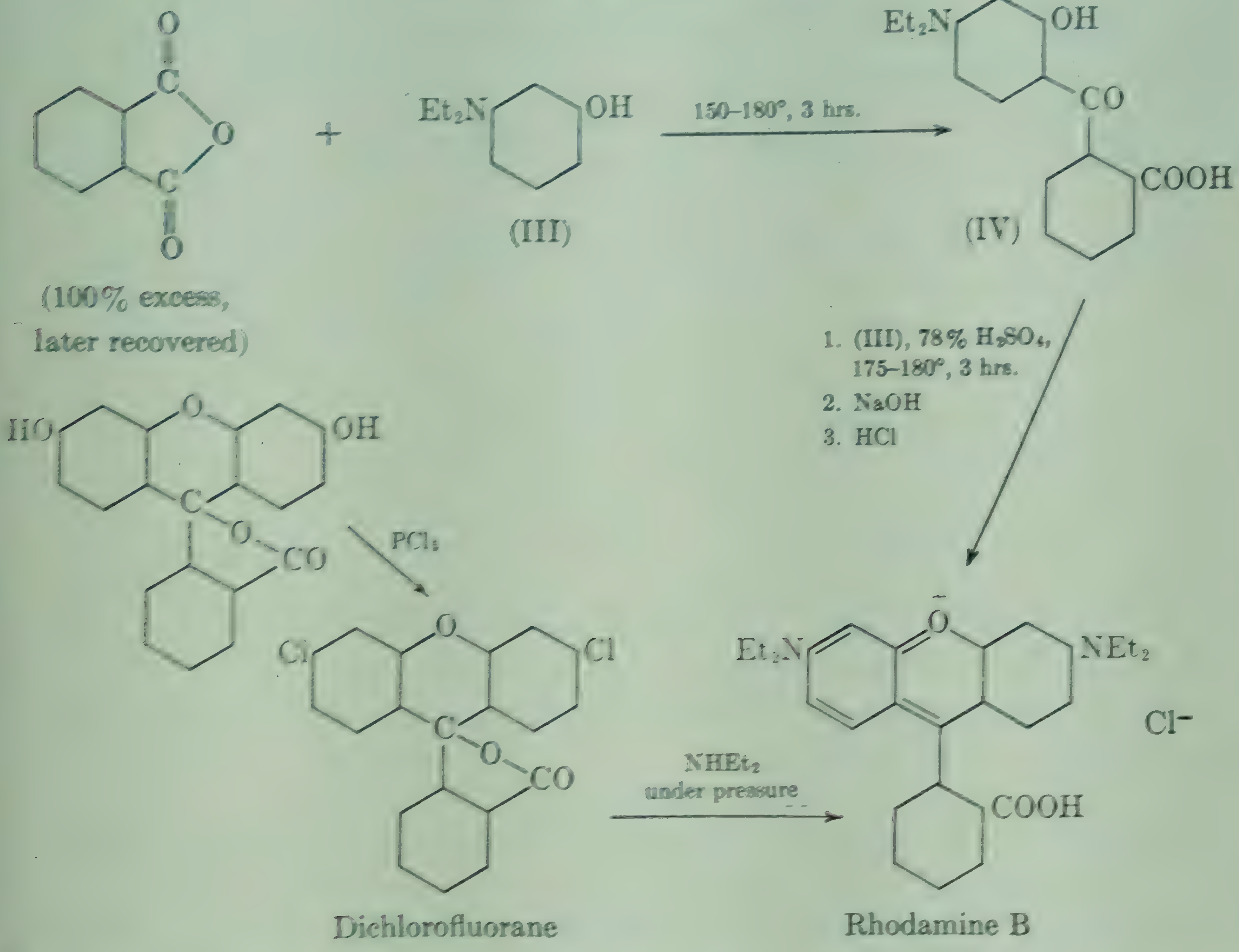
Chromogen Red B (IG) is a mordant dye of the phthalein as well as Rhodamine series; applied to chrome-mordanted wool, the shade has good fastness to light and milling.[6]



Chromogen Red B

Rhodamines. With the exception of Rhodamine S and 5G mentioned earlier, the Rhodamines are alkylamino derivatives of fluorane; ethyl derivatives are more soluble and are technically more valuable than the methyl derivatives. They are prepared by one of two methods: the condensation of a *m*-alkylaminophenol with phthalic anhydride, or the replacement of chlorine in dichlorofluorane by alkylamino groups. Thus Rhodamine B (Céresole, 1887) (BASF; CI 749) may be prepared directly from *m*-diethylaminophenol or indirectly from Fluorescein. The first method is used technically for the alkylamino derivatives such as Rhodamine B, and the second for the arylamino derivatives which are sulfonated to acid dyes. The two moles of *m*-dialkylaminophenol (III) condense in two stages; the intermediate benzoylbenzoic acid (IV) is not isolated, and the reaction is carried out progressively by the gradual addition of (III) and the introduction, at the appropriate stage, of the sulfuric acid necessary for the condensation of the second mole of (III). Rhodamine B finds considerable use, although it dyes unattractive bluish pink shades with poor fastness on wool and silk and on tannin-mordanted cotton; on the animal fibers the shades are strongly fluorescent; the dye is also used for coloring paper.[9] By the reaction of a basic dye, such as Rhodamine B, with a sodium alkyl sulfate (e.g., sodium cetyl or octadecyl sulfate) products are obtained which give fast dyeings after treatment with aluminum chloride, barium chloride and stannous chloride.[10] Rhodamine B and antimony compounds form a colored complex which can be used for the determination of antimony in biological fluids.[11]

CHART 1
Preparation of Rhodamine B


(100% excess, later recovered)
(III)
150–180°, 3 hrs.
(IV)
1. (III), 78% H_2SO_4, 175–180°, 3 hrs.
2. NaOH
3. HCl
PCl_5
NHEt$_2$ under pressure
Dichlorofluorane
Rhodamine B

The ethyl ester of Rhodamine B is the bluer Rhodamine 3B (Monnet, 1891) (BASF; CI 751). The esterification of the carboxyl group, a reaction also involved in the preparation of Rhodamine 6G and 6G extra, is carried out by heating the carboxylic acid in 94% alcohol solution with ethyl chloride and magnesium oxide at 120° (7–8 atmospheres pressure) in an autoclave for several hours. The ethyl ester of the phthalein from *m*-monoethylaminophenol is Rhodamine 6G (Bernthsen, 1892; Schmidt and Rey, 1892) (BASF; CI 752) which dyes the most beautiful shades among the dyes of this series and is highly prized in calico printing. The shades have good washing fastness, but low light fastness. The phosphomolybdotungstic lake is a valuable pigment, Fanal Pink (IG) (see Chapter XXIII). Rhodamine 6GP or 6G extra (IG), the higher homolog of Rhodamine 6G, is another beautiful and largely used dye. Rhodamine 3GO (IG) is made specially for the dyeing of silk; being unsymmetrically constituted, the phthalein condensation has to be effected in two stages.[6]

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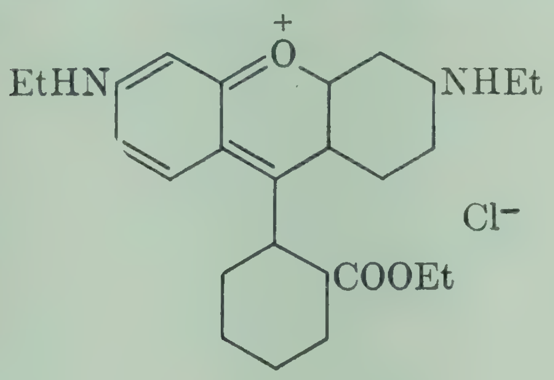
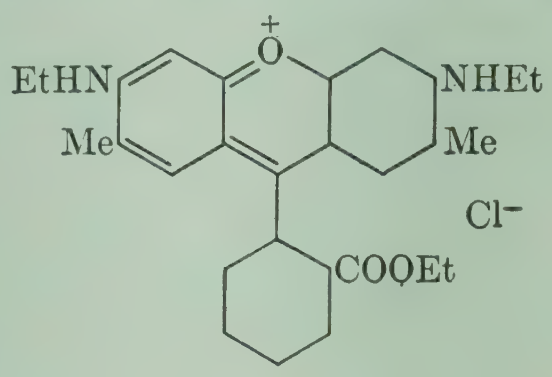
[9] For a study of chromium-Rhodamine B toners, see Schmutzler and Othmer, *Am. Ink. Maker* **26**, No. 4, 29 (1948).

[10] Lenher and du Pont, USP 2,052,716; du Pont, DRP 666,083.

[11] Maren, *Anal. Chem.* **19**, 487 (1947).

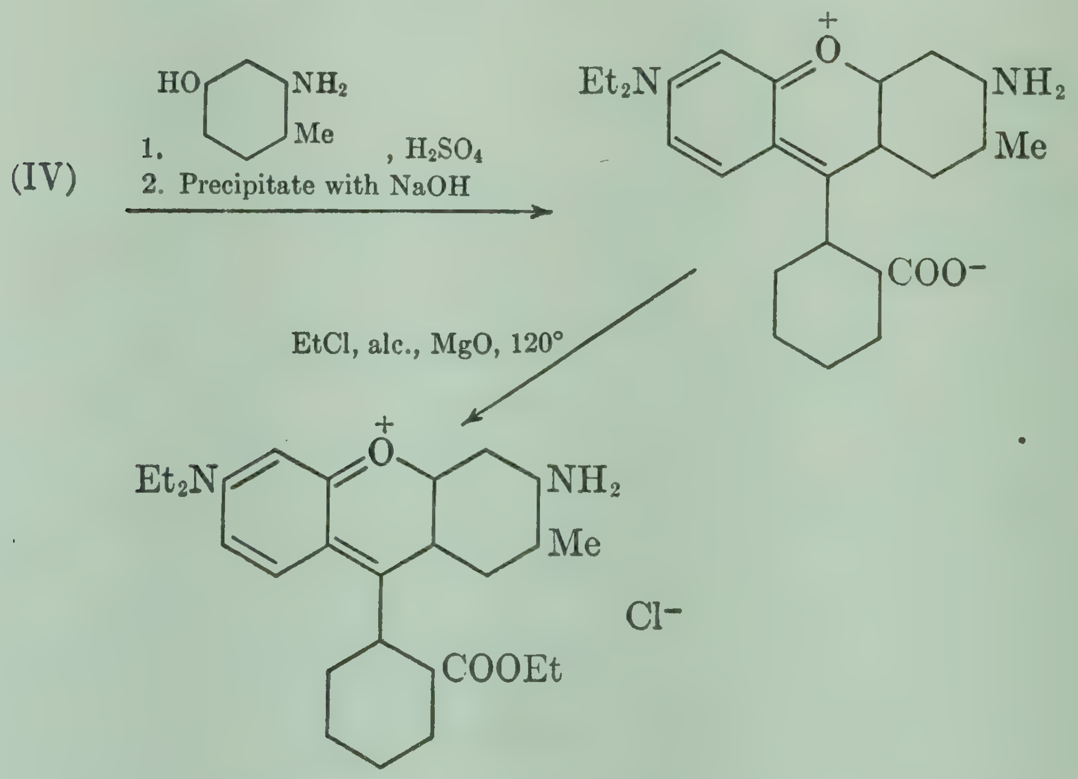


Rhodamine 6G



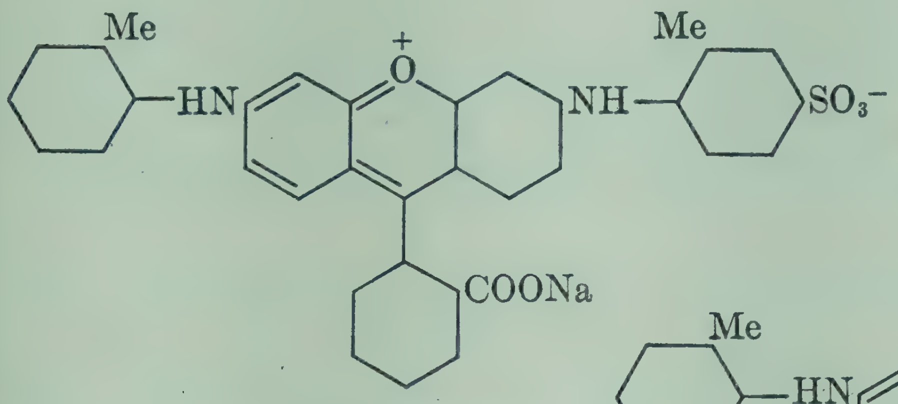
Rhodamine 6GP or 6G extra

CHART 2
PREPARATION OF RHODAMINE 3GO

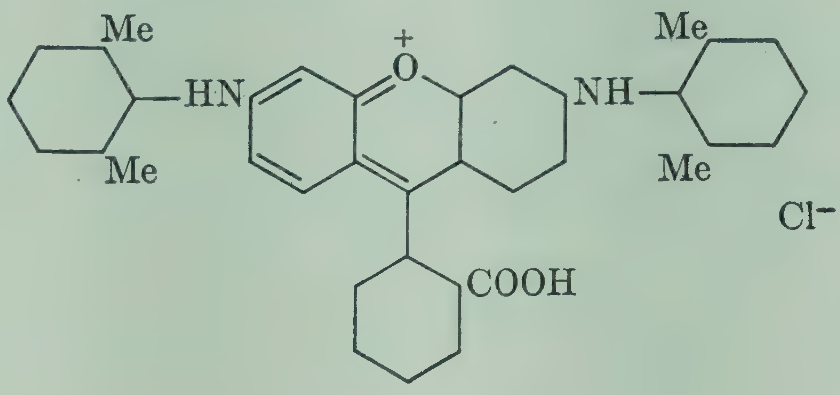


Rhodamine 3GO

Acid colors can be obtained by the introduction of sulfonic groups, but these are not prepared by sulfonating the basic Rhodamines so far described. Dichlorofluorane is condensed with a primary aromatic amine by heating in presence of zinc chloride and quicklime to about 200° for a few hours; and the product (obtained in nearly quantitative yield) is sulfonated. Using aniline and *o*-toluidine respectively, Fast Acid Violet B (Schmidt, 1888) (MLB; CI 757) and Acid Violet 4R (BASF) or Fast Acid Violet ARR (MLB; CI 758) are obtained. Fast Acid Blue R (MLB; CI 760) or Violamine Ia3BA (IG) is obtained similarly from *p*-phenetidine and the tetrachlorofluorane obtained from dichlorophthalic anhydride.[6] Dyes of this type have good fastness to light (5) and to milling (3–4). The unsulfonated compounds may be used as spirit-soluble dyes; e.g. Spirit Fast Violet R (IG) is dianilinofluorane, of which the corresponding sulfonic acid is Fast Acid Violet B or Violamine IaB.[6] The unsulfonated base of Acid Violet 4R is Spirit Fast Red 3B (IG). Violamine 3G spirit-soluble (IG) is the condensation product of two moles of *m*-2-xylidine with dichlorofluorane.[6] Sulfonated 3,6-dianilinofluoranes in which the anilino group contains *o*- or *p*-alkyl or cyclohexyl groups are red to violet wool dyes, faster to wet treatments than conventional xanthene dyes.[11a]



Acid Violet 4R



Violamine 3G

Chromoxane Brilliant Red BL is a Rhodamine with mordant dyeing properties, useful as a wool and silk dye and as a chrome printing color for cotton.[7] Like other dyes of the Chromoxane series, it has good all-round fastness. An interesting feature of the preparation of Chromoxane Brilliant Red BL is the use of hydroxytrimellitic acid (V), which is converted into the anhydride (VI) by heating with concentrated sulfuric acid in *o*-dichlorobenzene solution at 170–175°; *m*-diethylaminophenol is

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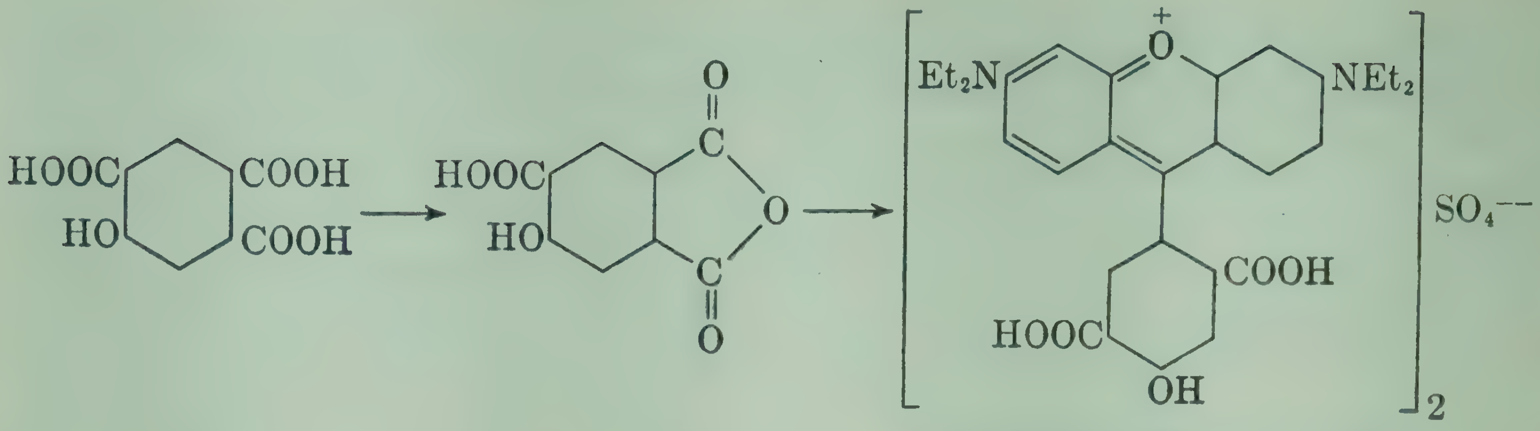
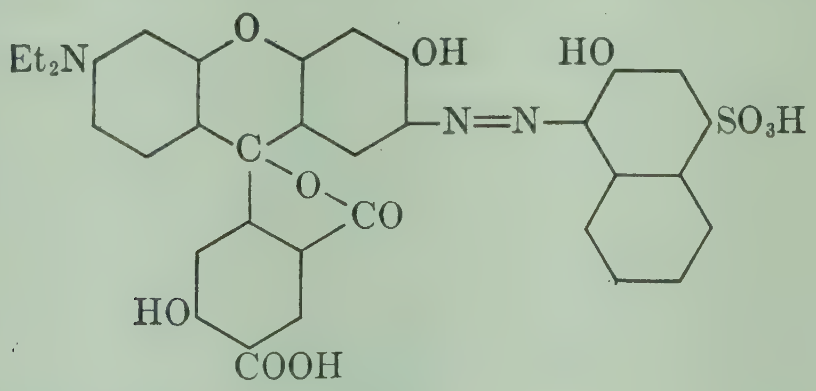
[11a] France, Haddock, and ICI, BP 631,039–40.



(V) (VI) Chromoxane Brilliant Red BL

added and the reaction continued till no more water distils over (about 5 hours).[7, 12, 13] Chromoxane Brilliant Red BD (3BD extra) is prepared by dissolving BL in hot aqueous sodium carbonate and salting out with rock salt.[7, 14]

By condensing (V) with resorcinol or chlororesorcinol, orange, brown and red chromable dyes are obtained.[15] The trimellitic acid series has been extended by using *N*-acylamidotrimellitic acids to condense with *m*-alkylaminophenols, giving orange, yellow and bluish red dyes.[16] Chloro- and bromotrimellitic acids have also been used for synthesizing xanthene dyes by condensation with two moles of *m*-diethylaminophenol.[17] The halogen atom can be replaced by a piperidino or dimethylamino residue or by hydroxyl,[18] the resulting bluish-red dyes can be afterchromed, and are suitable for cotton or viscose printing. More complicated dyes are obtained by condensing (VI) with one mole of a *m*-alkylaminophenol, and then with a monoazo dye derived from resorcinol and, for example, an aminonaphtholsulfonic acid or an aminosalicylic acid.[19] The products (e.g., VII) can be used as afterchrome dyes for wool, or for chrome printing on cotton and viscose.



(VII)

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[12] IG, BP 472,757; 477,605; 493,293.

[13] Buchler, Spees and Sanguinetti, *JACS* **71,** 11 (1949).

[14] *BIOS* Misc. Rept. **20.**

[15] IG, BP 495,260.

[16] IG, BP 516,930.

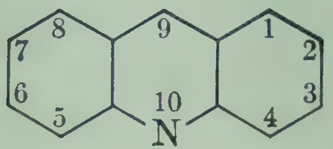
[17] IG, BP 508,856.

[18] SP 224,872.

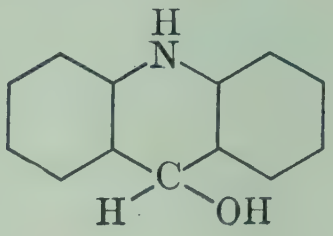
[19] IG, BP 480,328.

ACRIDINE DYES

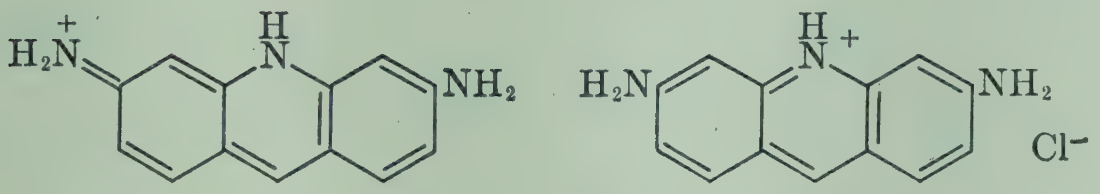
Although acridine is found in coal tar, and can also be readily synthesized from diphenylamine by condensation with formic or oxalic acid in presence of zinc chloride, the acridine dyes are made by *m*-diamine condensations analogous to the preparation of Pyronines from *m*-alkylaminophenols. The acridine dyes contain amino groups in the 3,6-positions, and are salts of 9-hydroxy-9,10-dihydroacridine (I). They are conveniently written in the *o*-quinonoid form; but like the azine, thiazine, oxazine and xanthene dyes to which they are structurally allied, the diaminoacridinium ions are resonance hybrids of structures such as (IIA) and (IIB).



Acridine



(I)



(IIA) (IIB)

3,6-Diaminoacridine hydrochloride

Like the xanthenes, the acridine dyes fall into two groups: diphenylmethane and triphenylmethane derivatives; but with the acridines the first type is more important, including Acridine Orange NO and valuable chemotherapeuticals. The acridine dyes as a whole constitute a small group of yellow, orange and brown basic dyes, which have a limited use in dyeing wool, silk and jute, in calico printing, and as leather dyes. As antiseptics and medicinals, the acridine derivatives have much greater interest.

Diphenylmethane derivatives. 3,6-Diaminoacridine sulfate is the antiseptic Proflavine, first made by Ehrlich and Benda (1910), and later by Freres (1919) by an improved method in which *m*-phenylenediamine is heated with glycerol, oxalic acid and zinc chloride at 190°, and the diaminodihydroacridine or leuco base thus formed is oxidized to the acridine.[20] Proflavine is then prepared by dissolving the diaminoacridine in sulfuric acid. 3,6-Diaminoacridine cannot be prepared by condensing *m*-phenylenediamine with formaldehyde, but an alternative route, starting from aniline and formaldehyde, is outlined in Chart 3. Benda (1912) also prepared pure 3,6-diamino-10-methylacridinium chloride, described originally in 1890; Ehrlich found that the compound is active against trypanosomes, and named it Trypaflavine (C; CI 790). Both Trypaflavine (Ehrlich and Benda, 1910) (C; CI 790) (now known as Acriflavine) and Proflavine are powerful antiseptic and bacteriostatic agents, and Browning's studies (1913) led to their extensive use as wound antiseptics in the first world war. Acriflavine is more potent than Proflavine, but also acts more slowly and is more toxic, and its use in preference to Proflavine appears to be irrational.[21] Trypaflavine (IG) is stated to be a mixture of pure Trypaflavine (63–67%), Proflavine (21.5–27.5%), 7–8% water and 2.5–3.5% of sodium chloride.[22] It is used in the treatment of various conditions requiring an external antiseptic. Acridine

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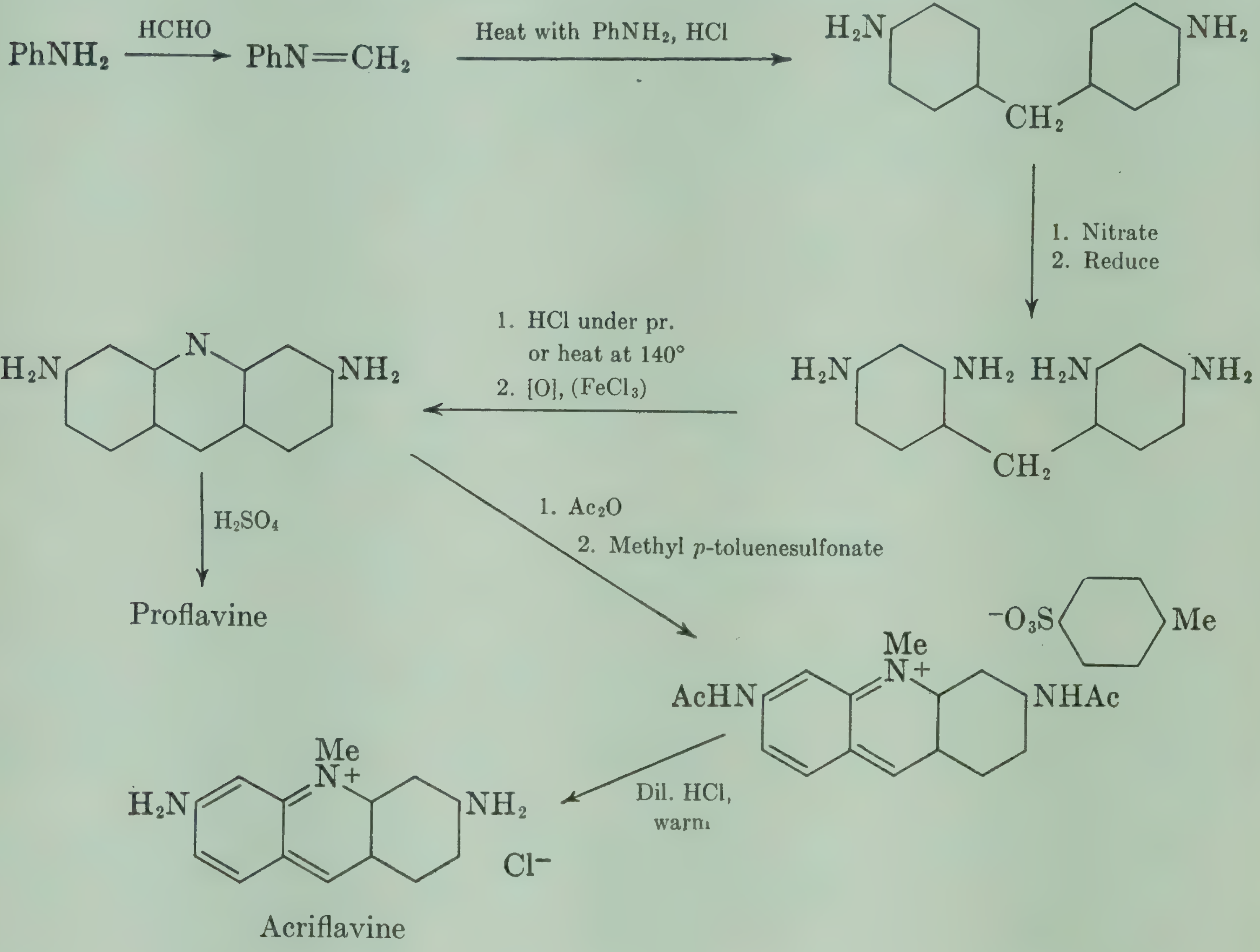
[20] Etablissements Poulenc Frères, DRP 347,819; see also Albert, *JCS* 121, 484 (**1941**).

CHART 3

Synthesis of Proflavine and Acriflavine


PhNH₂
HCHO
PhN=CH₂
Heat with PhNH₂, HCl
H₂N
NH₂
CH₂
1. Nitrate
2. Reduce
H₂N NH₂ H₂N NH₂
CH₂
1. HCl under pr.
or heat at 140°
2. [O], (FeCl₃)
H₂N N NH₂
H₂SO₄
Proflavine
1. Ac₂O
2. Methyl p-toluenesulfonate
⁻O₃S Me
Me
N+
AcHN NHAc
Dil. HCl,
warm
Me
N+
H₂N NH₂
Cl⁻
Acriflavine

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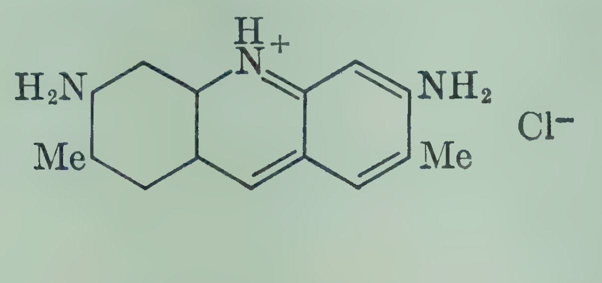
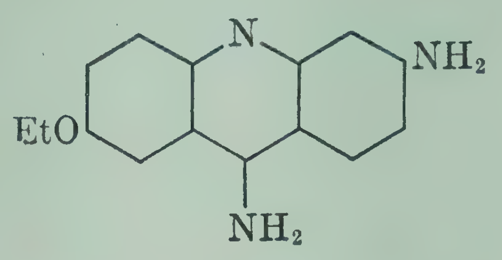
[21] Berry, *Quart. J. Pharm. Pharmacol.* **14,** 149 (1941).

[22] *FIAT* **868.**

Yellow G (Bender, 1889) (L; CI 785) is a homolog of Proflavine, prepared from *m*-toluylenediamine. It had some use at one time both as an antiseptic and as a dye. Auracine G (By; CI 786) is the formate of Acridine Yellow; the 10-methyl derivative of Acridine Yellow is Diamond Phosphine GF (IG).[6] Monoacyldiaminoacridines are of interest as fungicides.[23] Rivanol (Morgenroth, 1921) is a yellow dye, which has been used in the treatment of amoebic dysentery.



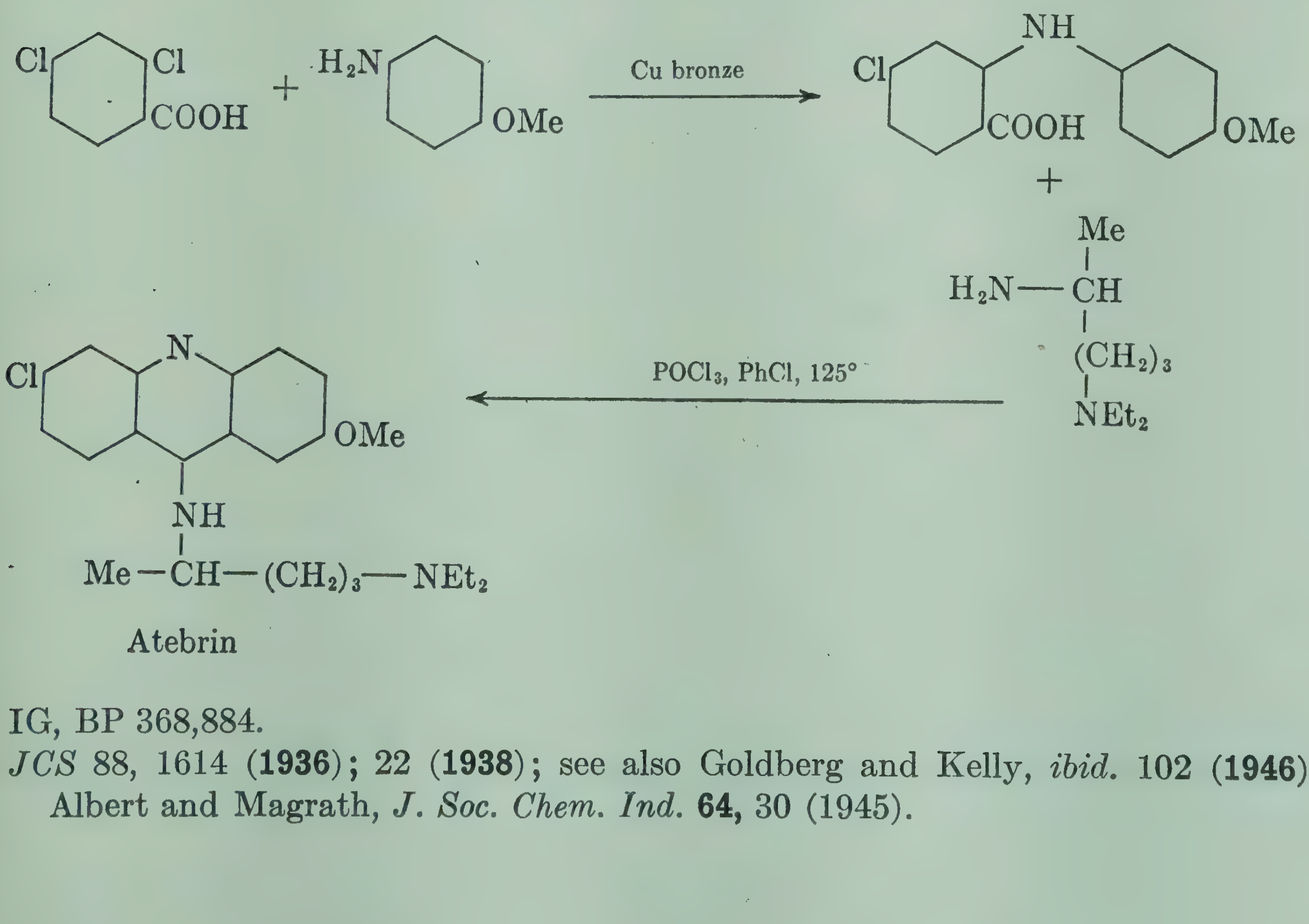
Acridine Yellow



Rivanol

Albert and Linnell[24] have studied the effect of the position of the amino groups in mono- and diaminoacridines on the bacteriostatic power. 9-Aminoacridine and 9-amino-4-methylacridine have a marked synergistic effect on the antibacterial action of the sulfanilamides.

Since quinine is a quinoline derivative and acridine is a benzoquinoline, acridine compounds have figured prominently in the search for antimalarials, and Atebrin (Mepacrine, Quinacrine) was introduced by IG in 1930. It is as effective as quinine and has the advantage of being better tolerated, so that it is particularly useful in cases where quinine is contraindicated. It is frequently administered in combination with Plasmochine which is a quinoline derivative having the same side chain



Atebrin

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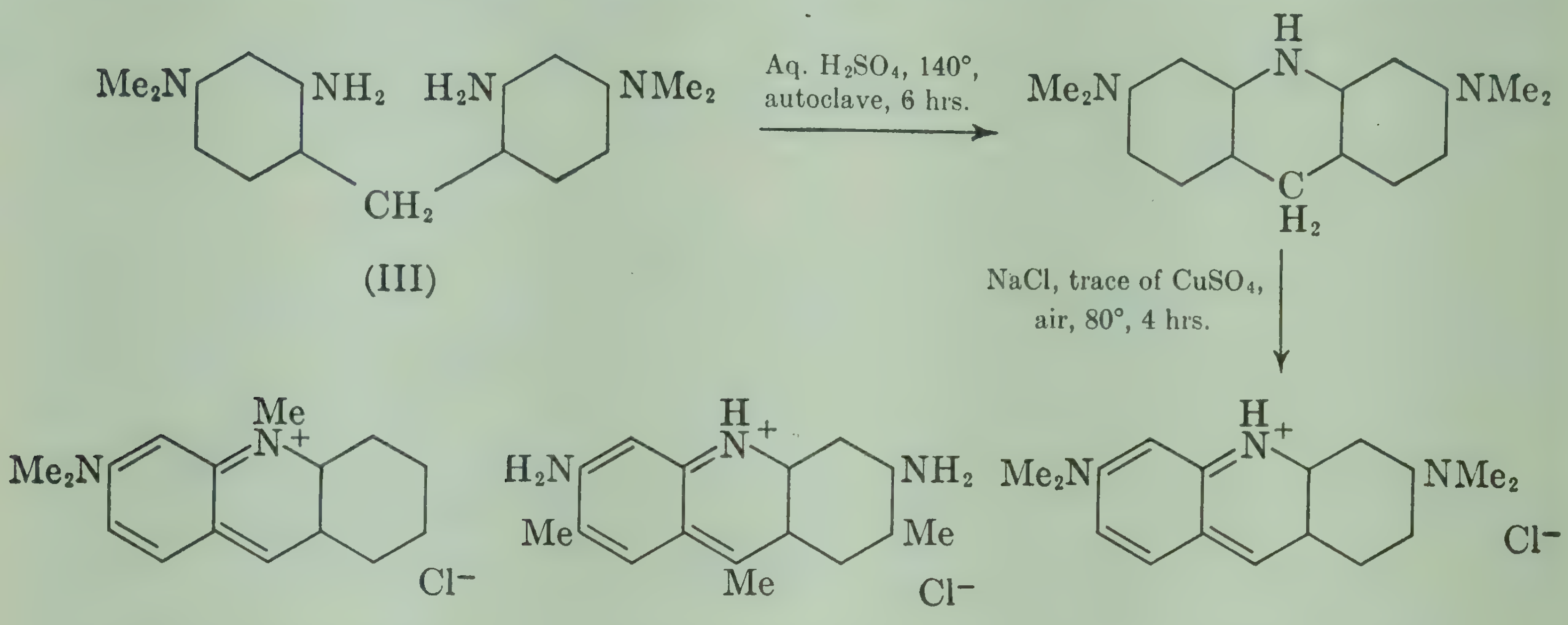
[23] IG, BP 368,884.

[24] *JCS* 88, 1614 (**1936**); 22 (**1938**); see also Goldberg and Kelly, *ibid.* 102 (**1946**); Albert and Magrath, *J. Soc. Chem. Ind.* **64,** 30 (1945).

as Atebrin. The starting materials for Atebrin are the dye intermediates, 2,4-dichlorobenzoic acid and *p*-anisidine.

Among the very few acridine dyes derived from diphenylmethane, which are of interest in dyeing, is Acridine Orange NO (Bender, 1889) (L; CI 788) or Rhoduline Orange NO (Euchrysine 3RX, IG).[6] Alternative methods are available for preparing the intermediate (III) which is cyclized and oxidized to the dye. *m*-Aminodimethyl aniline may be condensed with formaldehyde, or 4,4′-bis-dimethylaminodiphenylmethane may be nitrated and reduced. Acridine Orange NO dyes silk from


Aq. H_2SO_4, 140°, autoclave, 6 hrs.
NaCl, trace of $CuSO_4$, air, 80°, 4 hrs.

(III)

Diamond Phosphine RF

Euchrysine GGNX

Acridine Orange NO

a soap bath orange with a green fluorescence, and it is also used in calico printing and leather dyeing. Acridine Orange is converted into brown to violet-brown basic dyes by nitration, reduction and oxidation. Euchrysine GGNX (IG), used for dyeing vegetable tanned leather and for yellow discharges in calico printing, is prepared from the appropriate diphenylamine and acetaldehyde.[25] Diamond Phosphine RF (IG) is an example of an unsymmetrically constituted acridine dye. Coriphosphine 0 (CI 787), probably the hydrochloride of 3-amino-6-dimethylamino-2-methylacridine, has found use in the preparation of artificial gold thread ("zari" threads) in India; cotton or silk threads are plated with silver and then coated with a lacquer dyed a golden shade with Coriphosphine 0.

The alkylation of Acridine Yellow or of Benzoflavine (see later) by means of alcohol and mineral acid yields useful leather dyes, marketed under the names of Brilliant Phosphine, Patent Phosphine, etc. One of the Brilliant Phosphines, a dibenzyl derivative of Acridine Yellow, is prepared from 2-*N*-benzyl-*m*-toluylenediamine and formaldehyde.

Albert and Bird[26] have made a systematic study of the color and dyeing properties of the aminoacridines.

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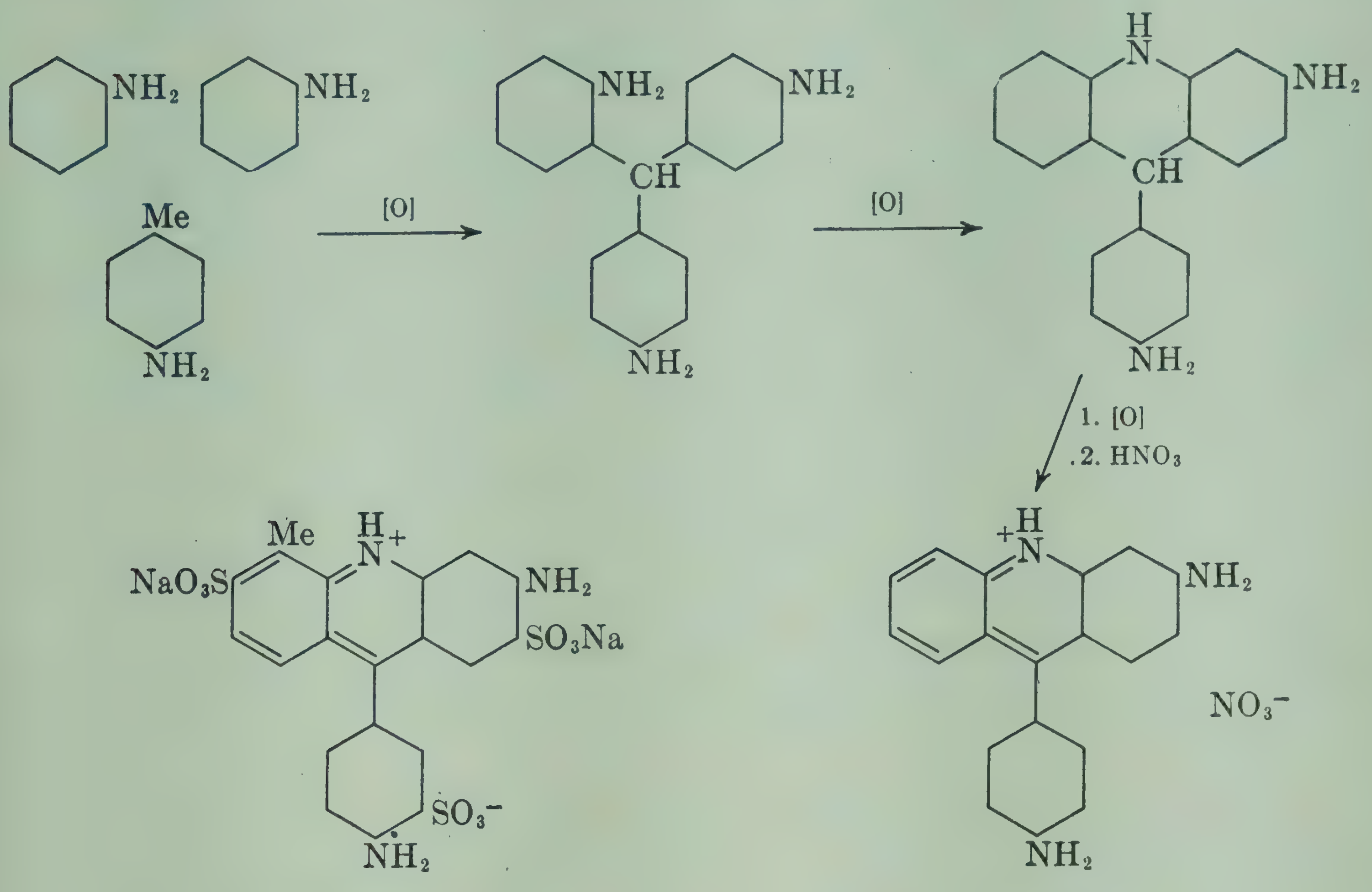
[25] *FIAT* **1313** II.

[26] *J. Soc. Dyers Colourists* **59,** 74 (1943); **64,** 357 (1948).

Triphenylmethane derivatives. The oldest member of the acridine class of dyes, Phosphine or Chrysaniline, a yellowish brown basic dye, was isolated as a by-product from the mother liquors of Magenta manufacture (Nicholson, 1862). It is still largely used in leather dyeing. The mechanism of its formation in the Magenta melt was determined by O. Fischer and Korner (1884). The constitution was confirmed by syntheses from *o*-nitrobenzaldehyde and aniline, and from *p*-aminobenzaldehyde and *m*-aminodiphenylamine. Sulfonation of Phosphine and its homologs gives useful leather dyes, e.g., Leather Yellow GS (IG).

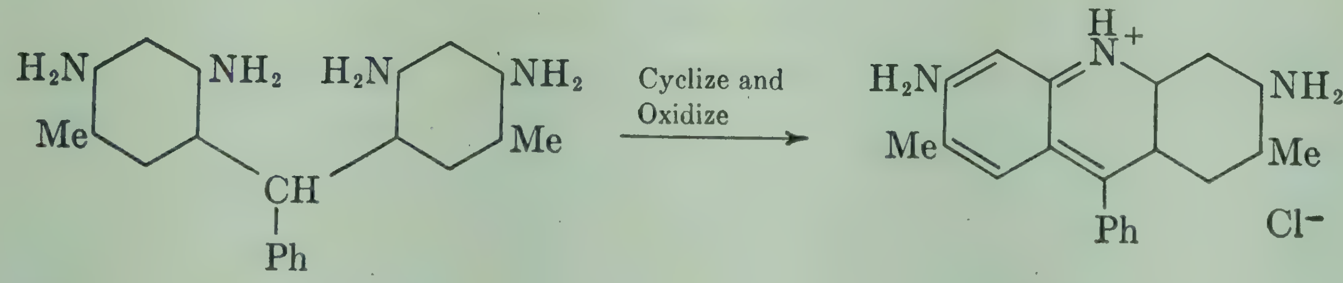


Leather Yellow GS

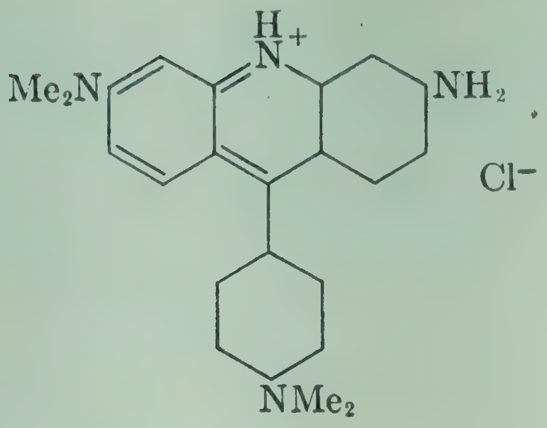
Phosphine

Benzoflavine (Rudolph, 1887) (GrE; CI 791) is prepared by condensing benzaldehyde with *m*-toluylenediamine to give the tetraminoditolylphenylmethane (IV), which is heated with hydrochloric acid under pressure for cyclization to the dihydroacridine and oxidized by means of air or ferric chloride. Benzoflavine is a yellow dye used in calico printing and leather

(IV)



Benzoflavine



Rheonine AL

dyeing. The reddish brown Rheonine AL (Muller, 1894) (BASF; CI 795) is used for similar purposes, and is made by the condensation of Michler's ketone with *m*-phenylenediamine. In applying these acridine dyes to leather, a potassium titanoxalate mordant is generally employed.[27]

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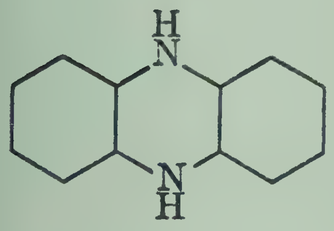
[27] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935.

Chapter XXV

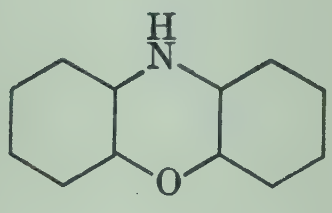
AZINES, OXAZINES, THIAZINES

The azine group is important in dyestuff history, since it includes Mauveine, the first coal-tar dye to be made commercially. Safranine and Induline, also azine dyes, were discovered soon after. Methylene Blue, the first technically useful thiazine dye, was made in 1876, and the first oxazine dye, Meldola's Blue, in 1879. The chemical constitution of these dyes, the mechanism of their formation and their interrelationships were, however, largely obscure for a quarter of a century, and were ultimately elucidated as a result of the work of several chemists: Witt, Nietzki, Bernthsen, Kehrmann, O. Fischer and Hepp.

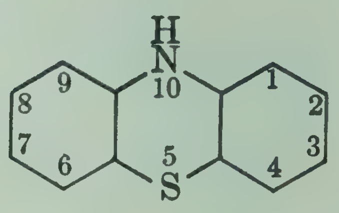
The parent ring systems from which the azine, oxazine and thiazine dyes are derived are dihydrophenazine (I), phenoxazine (II) and phenothiazine (III), so that the three series of dyes are very closely related in structure. The dyes themselves are "onium" salts of the general form (IV), in which X = NR, O or S. The basic dyes belonging to these three groups, as well as the xanthene and acridine dyes, can all be derived from the fundamental skeleton (V) by suitable changes in X and Y.[1] There has been considerable controversy in the past regarding the *o*- or *p*-quinonoid structure of these dyes, but it is now obvious that the cations are resonance hybrids, best represented in the form (IV). For the sake of simplicity, however, all the dyes in the series have been represented by structures in which the cationic charge is on a nitrogen, oxygen or sulfur atom in the heterocyclic ring. The deep and intense colors of the azine, oxazine and thiazine dyes are associated with a resonance



(I)



(II)



(III)

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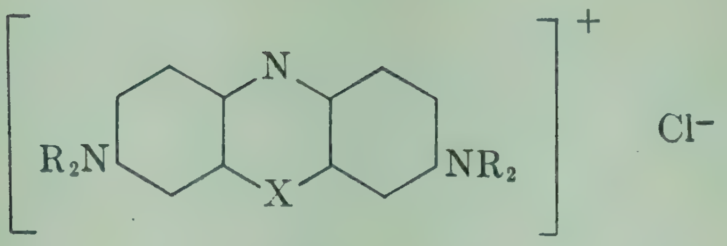
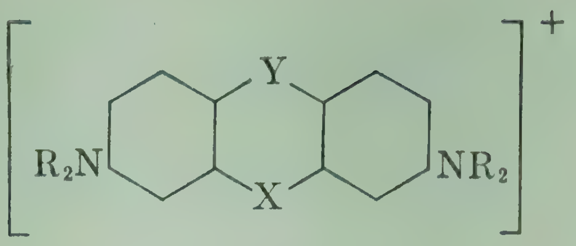
[1] See Chapter VIII.



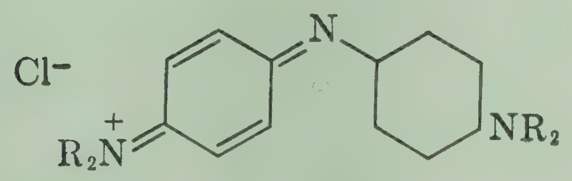
(IV)



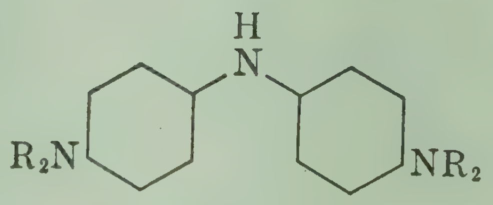
(V)

which is somewhat similar to the resonance to which the color of the triphenylmethane dyes is due, and this structural analogy between the two groups of dyes is also noticed in the similarity of the shades (brilliant reds, violets, blues and greens).[1]

The relationship of the azine, oxazine and thiazine dyes to indamines (VI) and leuco indamines (diphenylamines) (VII) is clear from an inspection of the formulas; the essential reaction involved in the conversion is cyclization by the introduction of a nitrogen, oxygen or sulfur atom. The azine, oxazine and thiazine dyes are mainly basic dyes, but as in the triphenylmethane series, the introduction of sulfonic groups, by sulfonation of the dye bases or by starting with intermediates containing sulfonic groups, leads to acid colors with improved fastness to light. The oxazine series has been extended more recently by the preparation of acid-mordant dyes, useful both as wool and silk dyes and as chrome-printing colors for cotton, and of direct cotton colors characterized by excellent fastness to light.[2–4]



(VI)



(VII)

QUINONEIMINES

The quinoneimines include blue and green compounds which are no longer employed as dyes, but they are closely related to azine, oxazine and thiazine dyes, and they are important intermediates for sulfide and sulfurized vat dyes.[5]

The indamines (e.g., Phenylene Blue) are obtained by oxidizing a neutral solution of one mole of a *p*-diamine (e.g., *p*-phenylenediamine), containing at least one primary amino group, and one mole of a monamine (e.g., aniline) having a free *p*-position. A second method is to condense

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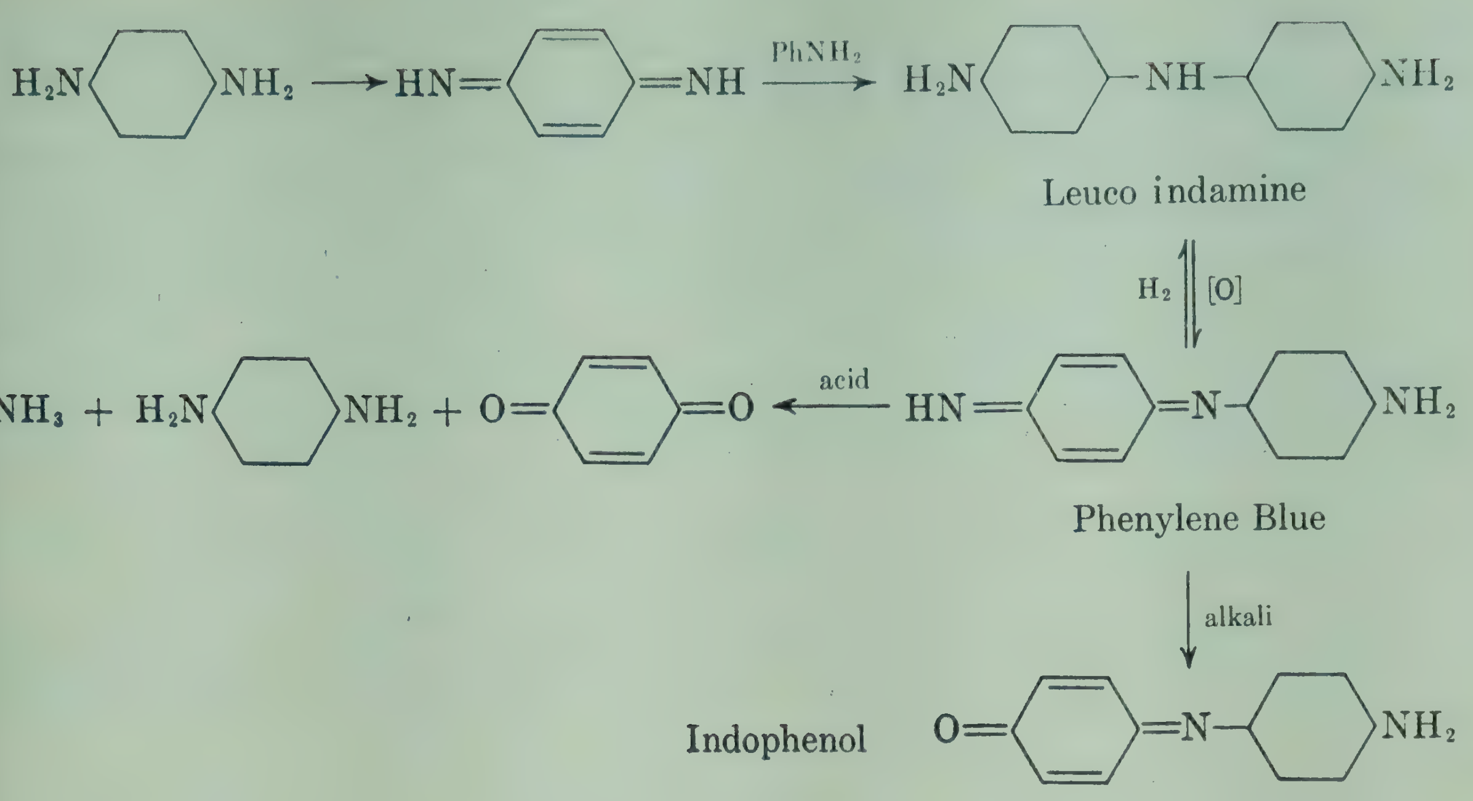
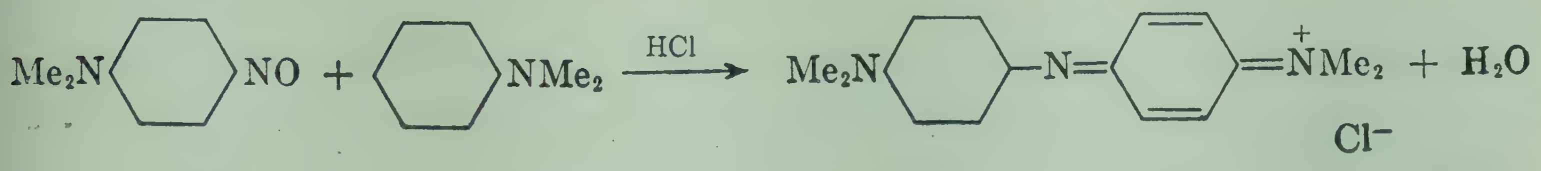
[2–4] IG methods of preparation of various azine, oxazine and thiazine dyes are described in (2) *BIOS* **959**, (3) *FIAT* **1313** II, and (4) *BIOS* **1433**.

[5] See Chapters XXXV and XXXVI.

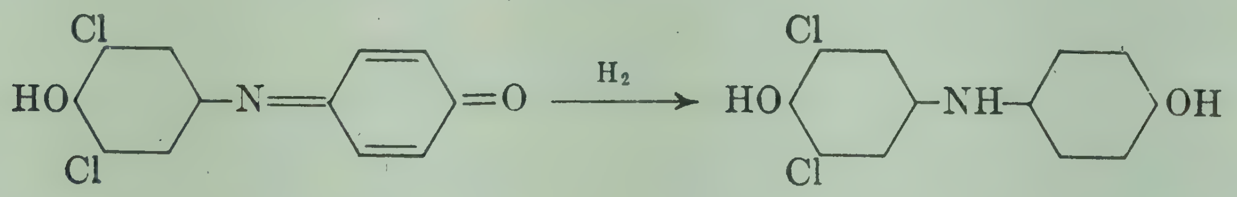

PhNH₂
Leuco indamine
H₂
[O]
acid
Phenylene Blue
alkali
Indophenol

a nitroso compound with a tertiary amine. The indamines are readily reduced to the leuco compounds (4,4′-diaminodiphenylamine and its derivatives).

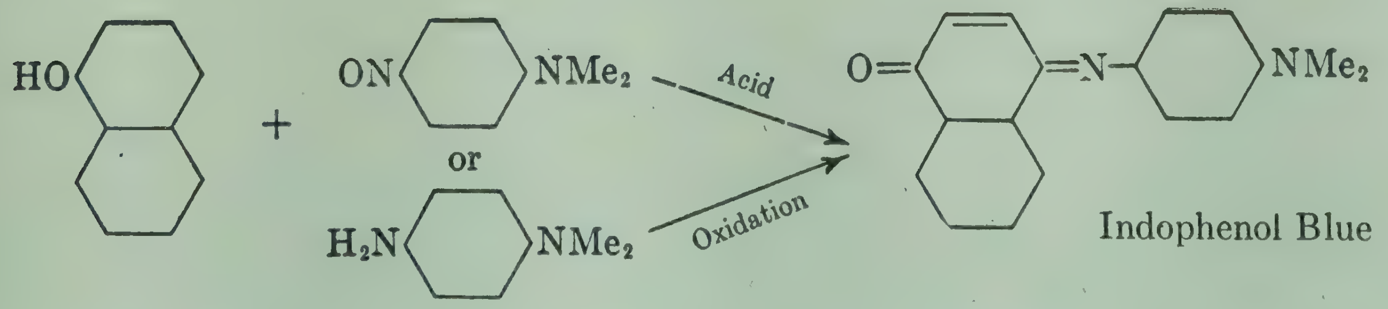


The indamines are also sensitive to both acid and alkaline hydrolysis. Alkaline hydrolysis leads to the indophenols, sometimes called indoanilines to distinguish them from the "true indophenols" (e.g. I).

(I)



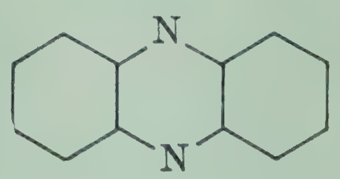
However, indophenols of the type (I), which is an oxidizing agent (Tillmans reagent) used for the estimation of ascorbic acid and is also an indicator (blue with alkali, red with acid), do not figure as dye intermediates.


or
Acid
Oxidation
Indophenol Blue

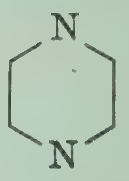
The term indophenol, therefore, usually represents the indoanilines in dyestuff chemistry. The indophenols are prepared by methods analogous to the two indicated for the indamines, with the difference that one of the reactants has a hydroxyl in place of an amino group.[5] Thus Indophenol Blue can be prepared by condensing α-naphthol with *p*-nitrosodimethylaniline, or by the oxidation (e.g., with dichromate and acetic acid) of a mixture of α-naphthol and *p*-aminodimethylaniline. The leuco compound in alkaline solution has affinity for cotton and Indophenol Blue was used at one time as a vat dye. Such indophenols can be used as fat-soluble dyes.

AZINES

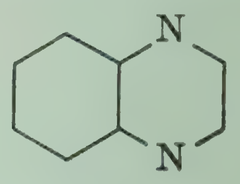
The parent ring system (I) from which dyes of this group are derived is known as phenazine or simply as azine, although the systematic name



(I)

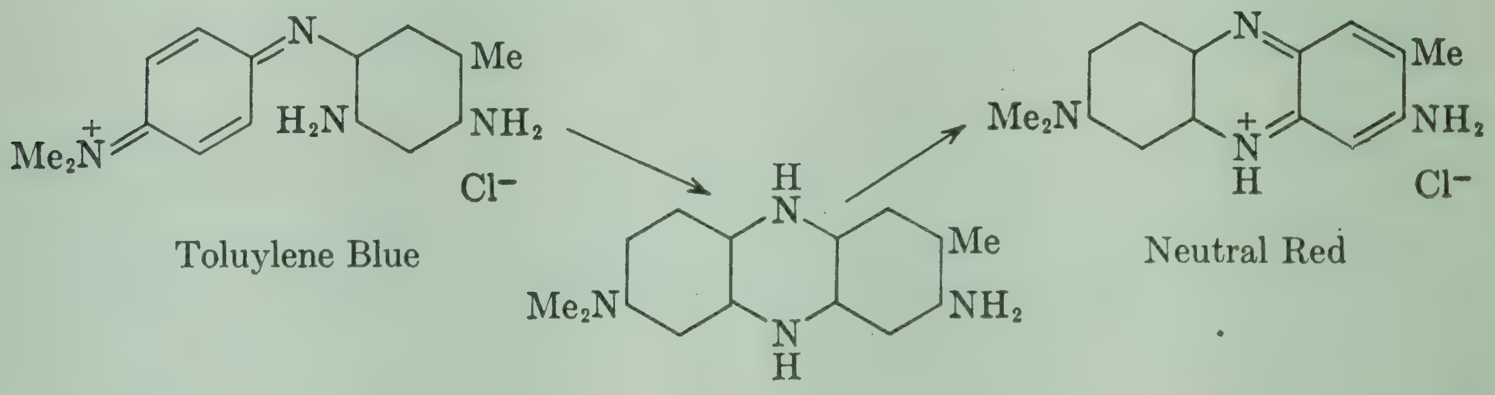


(II)



(III)

should be dibenzopyrazine, bearing the same relationship to pyrazine or 1,4-diazine (II) and quinoxaline (III) as anthracene to benzene and naphthalene. The azines[6] themselves are colorless or pale yellow compounds, but they form intensely colored salts, derivatives of phenazonium chloride, which are basic dyes. An interesting example of a dihydrophenazine with very different dyeing properties is the anthraquinonoid vat dye, Indanthrene Blue R.



Toluylene Blue

(IV)

Neutral Red

Intramolecular quinonoid addition in an indamine, such as Toluylene Blue (CI 820), results in a leuco azine (IV), which then undergoes oxidation to the azine (e.g., Neutral Red; CI 825). Neutral Red is readily obtained by adding *p*-nitrosodimethylaniline to a solution of *m*-toluylenediamine in hydrochloric acid containing a little ferrous chloride at 90–95°. Such phenazine dyes, not carrying an alkyl or aryl group on an azine nitrogen atom, have been classified as Eurhodines, and analogous compounds containing hydroxyl groups as Eurhodols. The Eurhodines and Eurhodols are obsolete as dyes, but Neutral Red is useful as an indicator (red to orange at pH 6.8–8.0) and as a microscopical stain.

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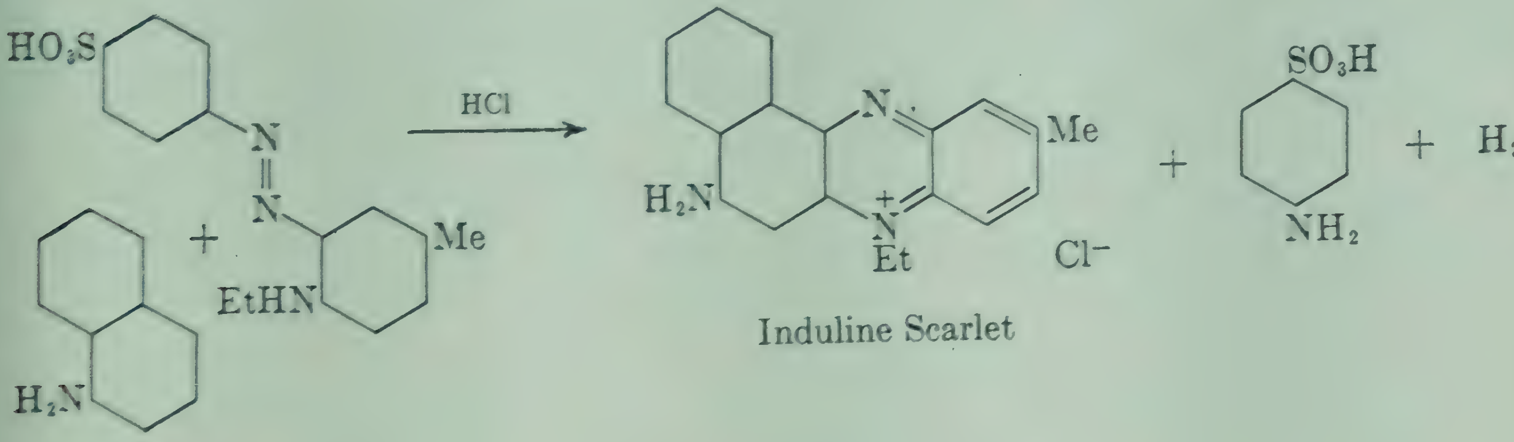
[6] Mason in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. I, Longmans, London, p. 563.

Another method of preparing an azine dye is to heat an *o*-aminoazo compound with an amine having a free *p*-position; thus the interaction of 2-ethylamino-5-methylazobenzene-4′-sulfonic acid with α-naphthylamine hydrochloride in presence of phenol as a diluent yields Induline Scarlet (CI 827), which was for a long time used as a catalyst in the preparation of the indigo vat and for printing vat colors by discharge methods in conjunction with formaldehyde sulfoxylate, but has now been displaced by anthraquinone. Azines of this type are called alkylrosindulines.

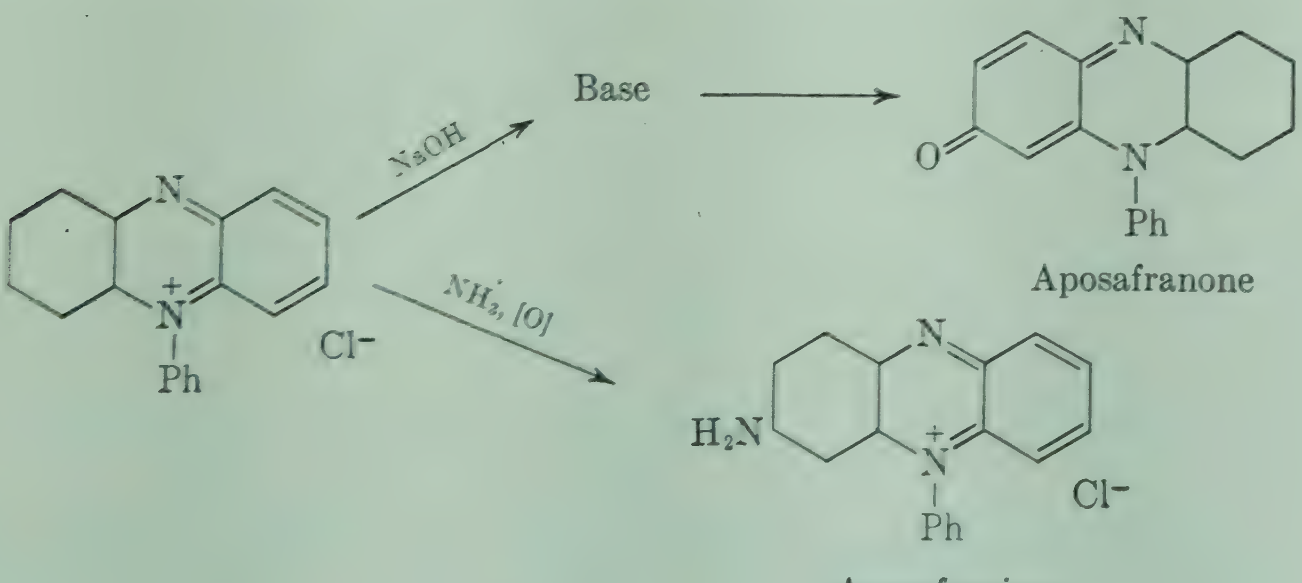


Induline Scarlet

SAFRANINES

The technically important azines are derivatives of 10-phenylphenazonium chloride (I). The monoamino compounds are sometimes called Aposafranines; aminohydroxy compounds Safraninoles; diamines Safra-

(I)

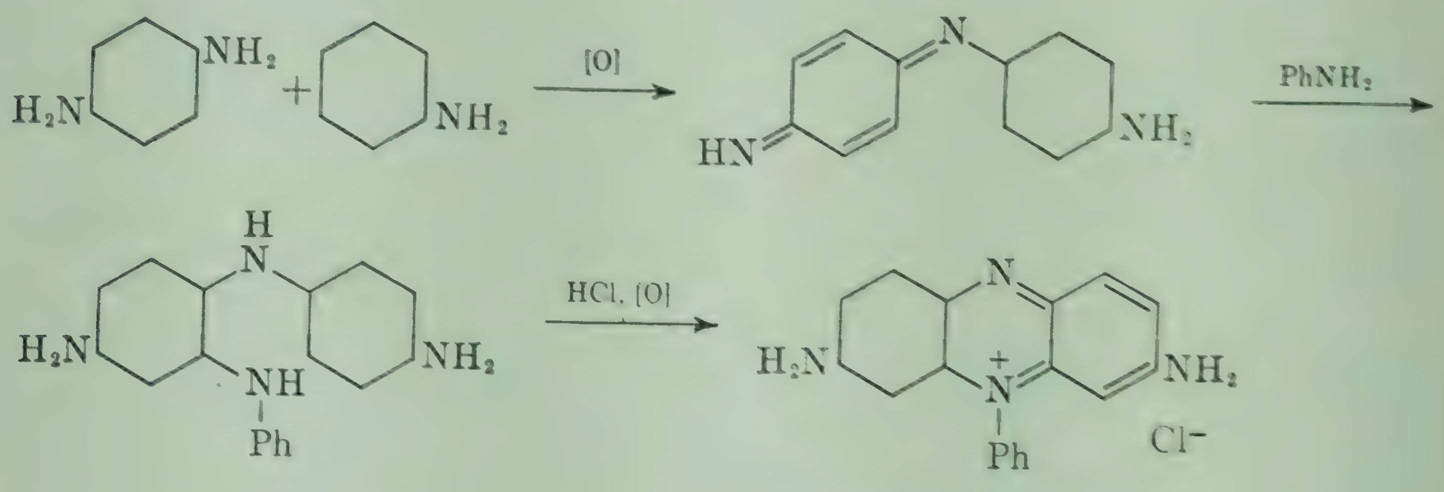


Aposafranone

Aposafranine

nines; and dihydroxy derivatives Safranoles. Although (I) is a strongly ionizing ammonium salt, the corresponding base is unstable, since (I) is converted by caustic alkali into Aposafranone and by ammonia into Aposafranine. This unusual amination is of interest from the point of view of the formation of Indulines and Nigrosines (see later). The accepted constitution of the Safranines is the result of Kehrmann's extensive work on the subject.[7]

The simplest Safranine (Safranine B; Phenosafranine; CI 840) is obtained by oxidizing a mixture of *p*-phenylenediamine and aniline to the indamine by means of dichromate and hydrochloric acid, and boiling the solution to convert the blue indamine into the red Safranine. The reactions involve the formation of an indamine, quinonoid addition of a molecule of aniline to form the *o*-anilinodiphenylamine derivative (II), which then undergoes oxidation to the Safranine. This is a general reaction, and is the method employed for the technical preparation of the Safranines. The requirements are one mole of a *p*-diamine and two moles of the same or different monamines; the *p*-diamine must have a free *o*-position and the monamine a free *m*-position for the cyclization to the azine to take place; this monamine must also have the *p*-position free for the indamine formation. The second monamine must be a primary amine. Among the oxidizing agents employed are ferric hydroxide, chromic acid and manganese dioxide sludge obtained as a by-product from saccharin manufacture.[8] Safranine B has been displaced by Safranine T in dyeing, but has found use as a photographic desensitizer, which enables panchromatic plates to be safely developed in diffuse light. The Safranine of commerce, Safranine T (G. Williams, 1859) (BASF; CI 841), consists largely of the higher homolog prepared from a crude



(II)

Safranine B (Phenosafranine)

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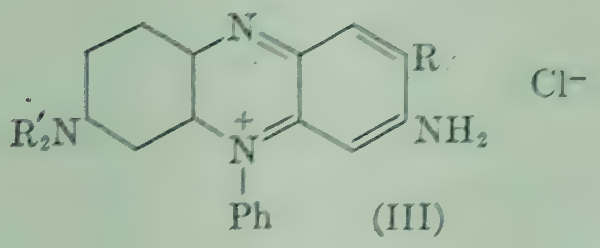
[7] Kehrmann *et al.*, *Helv. Chim. Acta* **8**, 675 (1925) and earlier papers.

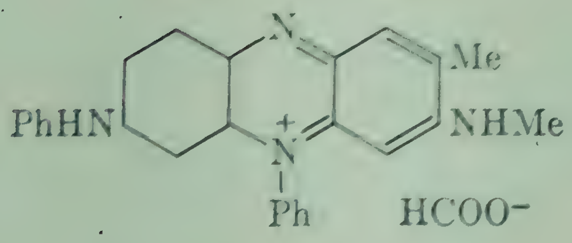
[8] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935, p. 321.

o-toluidine containing aniline; this is treated with a limited amount of nitrous acid to convert the primary amines partly into the aminoazo compounds which are reduced in situ with iron and acid to a mixture of aniline, *o*-toluidine, *p*-phenylenediamine and *p*-toluylenediamine. This mixture of mono- and diamines then undergoes the indamine oxidation and the azine cyclization. Safranine T extra conc. is a symmetrically constituted and substantially homogeneous compound prepared by reducing *o*-aminoazotoluene to *o*-toluidine and *p*-toluylenediamine, oxidizing with dichromate and hydrochloric acid, adding aniline, neutralizing with calcium carbonate and boiling.[3] The dye is purified by treatment with dichromate and sulfuric acid at 95°, making alkaline with soda ash and adding sodium sulfide. The mixture is filtered, and the filtrate salted out. Safranine T dyes tannin-mordanted cotton brilliant red shades with good fastness to washing and poor light fastness. One of the amino groups in Safranine is readily diazotizable, and the diazonium salts may be coupled with suitable components to give azo dyes with basic dyeing properties, such as Janus Blue G (MLB) or Indoine Blue (Kegel, 1886) (BASF; CI 135) (Safranine → β-Naphthol); but these have no technical value. The second amino group in Safranines can also be diazotized by using special methods (e.g., diazotization in concentrated sulfuric acid).

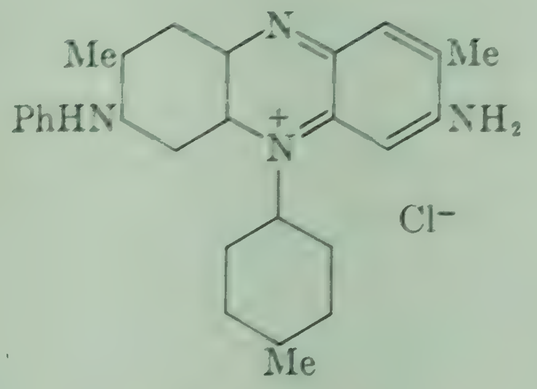
By oxidizing a mixture of *p*-aminodimethylaniline (or *p*-aminodiethylaniline) and aniline, Methylene Violets (III; R = H or Me; R^1 = Me or Et) are obtained; Safranine MN (CI 843) is (III; R and R^1 = Me).



(III)



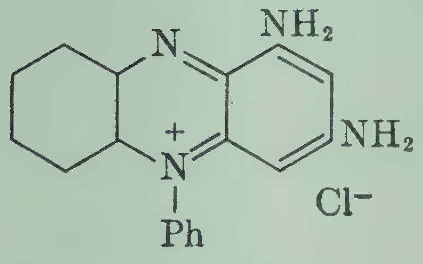
Rhoduline Heliotrope 3B



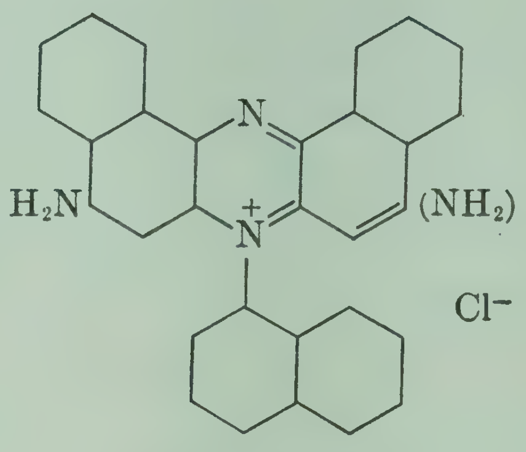
Mauveine

The tetramethyl and tetraethyl derivatives (Amethyst Violets; CI 847) are photographic desensitizers. Perkin's Mauveine, which was used for printing Victorian violet stamps and which has no technical interest at the present time, has been shown to be mainly constituted as phenylated tolusafranine. Rhoduline Heliotrope 3B (IG) is a dye of definite constitution prepared by oxidizing a mixture of *p*-aminodiphenylamine and monomethyl-*o*-toluidine to the indamine, condensing with aniline, and isolating the dye as the formate.[9]

Pinakryptol Green, which is isomeric with phenosafranine, is a powerful and widely used desensitizer for photographic films and plates.[10]



Pinakryptol Green



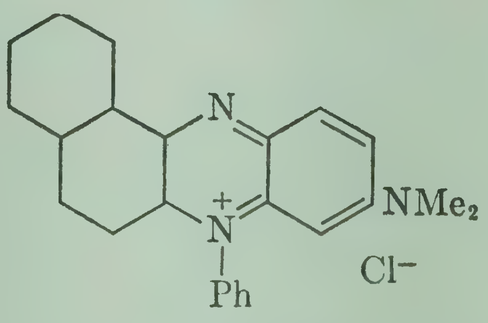
Magdala Red

The naphthalene analog of Safranine B, Magdala Red (DH; CI 857) is prepared by heating 4-aminoazonaphthalene hydrochloride and α-naphthylamine; it dyes silk a fluorescent pink shade.

Kehrmann[11] has utilized the condensation of 1-chloro-2,4-dinitronaphthalene with *o*-aminodiphenylamines for the preparation of azine dyes.[12]

The phenylnaphthophenazine derivatives such as the Azocarmines (see later) are sometimes classified as Rosindulines or Phenylrosindulines. A further distinction has been made between Rosindulines like the Azocarmines, which have the auxochrome in the naphthalene ring, and *iso*Rosindulines, such as Neutral Blue (C; CI 832), in which the auxochrome is in the benzene part of the naphthophenazine nucleus. These

Neutral Blue



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[9] Report 19, Textile Series, Office of the Quartermaster General, U.S. Dept. of Commerce.

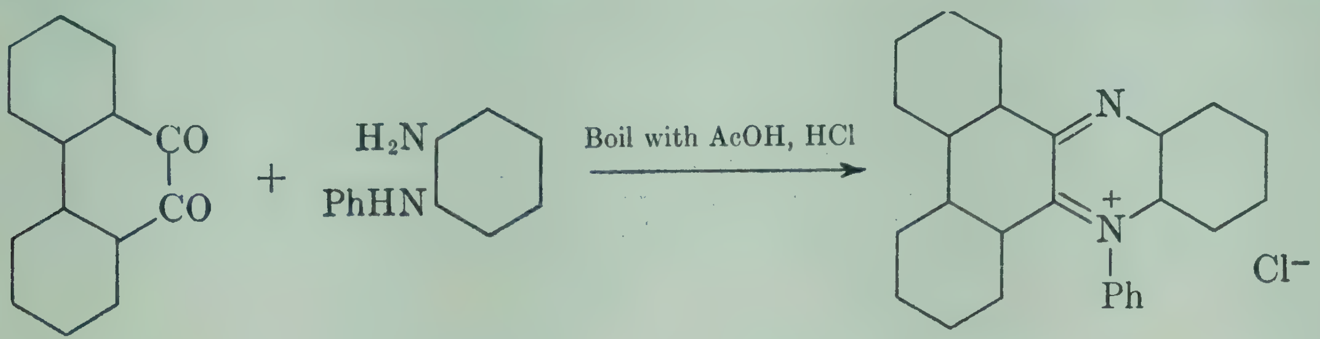
[10] See Chapter XXXVIII; and Mees, The Theory of the Photographic Process, Macmillan, New York, 1945, p. 1045.

[11] Kehrmann, *Ber.* **56**, 2385 (1923).

[12] For a summary of various methods for the preparation of azine dyes, see Lantz, *Ann. Chim.* (xi), **2**, 55, 101 (1934).

names, however, are confusing and serve no useful purpose; the chemistry of the Safranine series is readily understood by relating them to the parent phenylphenazonium chloride (I).

While the azine (I) has no dyeing properties, which are acquired only when one or more auxochromic amino groups are introduced, Flavinduline O (Schraube, 1893) (BASF; CI 824) is a brownish yellow basic dye, used at one time in calico printing and leather dyeing; it is prepared by condensing phenanthraquinone with *o*-aminodiphenylamine. Yellow to brown hydroxy- and aminophenanthranaphthazines have been prepared by the condensation of 1,2-naphthylenediamine (or its 5-sulfonic acid) with amino- and hydroxyphenanthraquinones; naphthaflavindulines containing bromo, amino and anilino groups dye wool in maroon, blue, and olive-green shades.[13]



Flavinduline O

Properties and reactions of the azines. The parent azines and the azine dyes give characteristic colorations with strong mineral acids, which change on dilution. Safranine forms a picrate which is insoluble in water, and readily soluble in chloroform, and Safranine can be estimated by titrating an aqueous solution with picric acid solution in presence of chloroform until the aqueous solution is decolorized.[14] Hydrolysis of azine dyes by heating under pressure with hydrochloric acid in glacial acetic acid gives hydroxy compounds, the absorption spectra of which give an indication of the constitution of the dyes.[15] Reduction and oxidation do not yield identifiable products.

The azine dyes are oxidation-reduction indicators, and the characteristic constants of the systems have been determined for several dyes (e.g., Neutral Blue; Induline Scarlet; Safranine B and T).[16] α-Hydroxyphenazine and Rosinduline are reduced in acid solution in two stages with the addition of one hydrogen atom in each case, the color changes (green → yellow; and violet → yellow) corresponding with the formation of semiquinones, which are true reduction products.[17]

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[13] Sircar and Dutt, *JCS* **121,** 1944, 1952 (1922).

[14] Castiglione, *Z. anal. Chem.* **97,** 334 (1934).

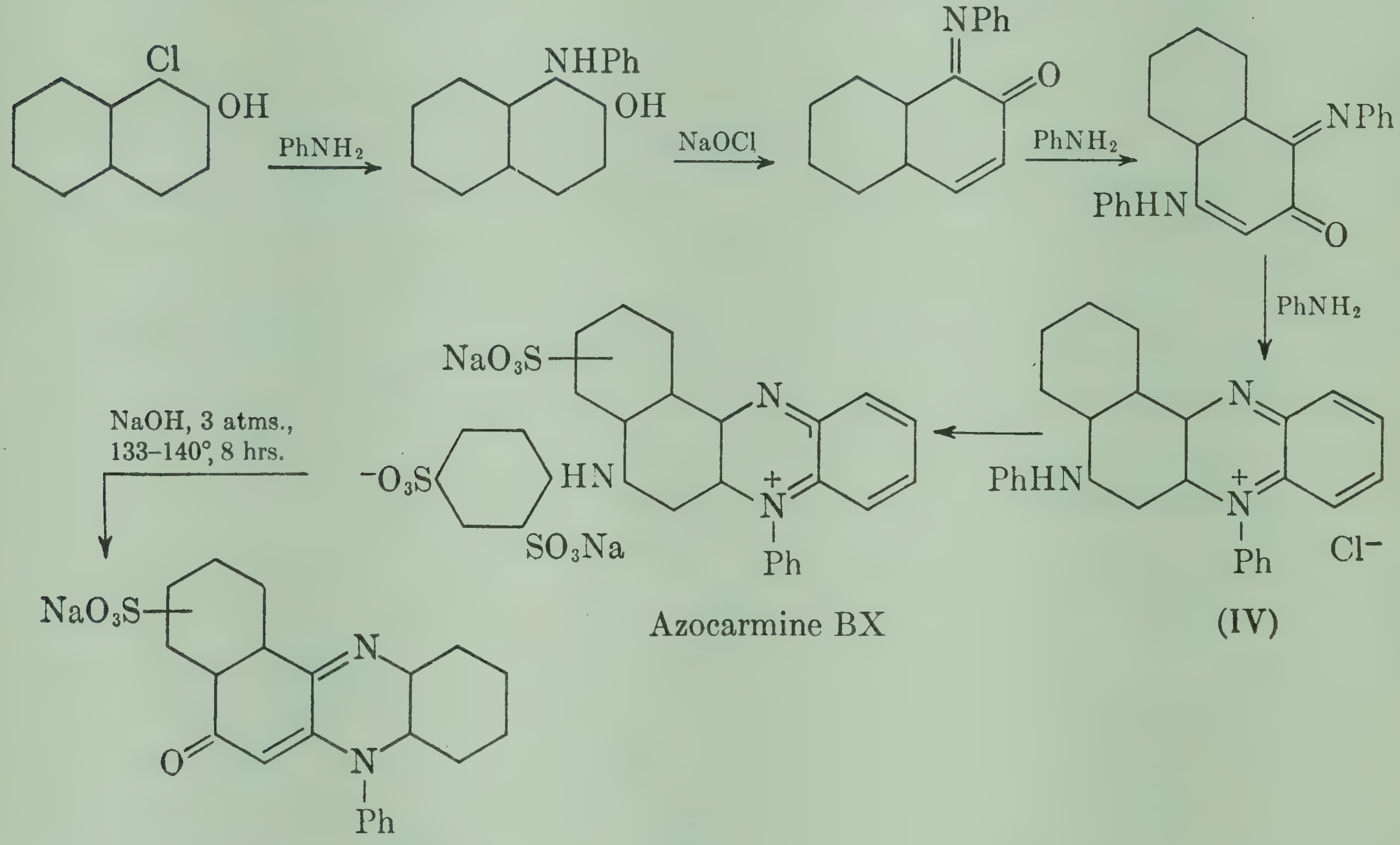
[15] Bass, *Helv. Chim. Acta* **16,** 403 (1933).

[16] Stiehler, Chen, and Clark, *JACS* **55,** 891, 4097 (1933).

[17] Michaelis, *J. Biol. Chem.* **92,** 211 (1931).

Mercurated Safranines, and compounds of Safranines with tannin, have been stated to have chemotherapeutic properties, the latter in the treatment of protozoal diseases.

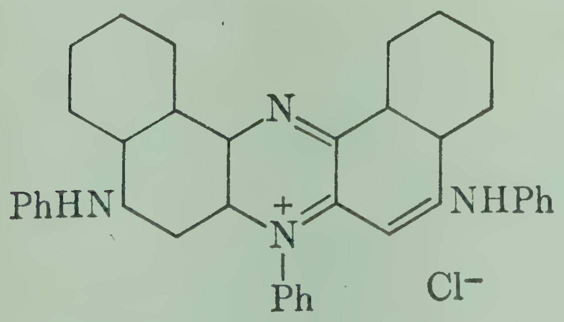
Acid dyes. 1-Chloro-2-naphthol is used as the starting material in a method[18] for the preparation of a phenylnaphthophenazine derivative (Azocarmine base; IV), which is obtained in nearly theoretical yield and in sufficient purity to be directly sulfonated; (IV) was originally prepared (1888) by fusing 4-benzeneazo-1-naphthylamine with aniline and aniline hydrochloride. Sulfonation gave the disulfonic acid (Azocarmine G; CI 828) and trisulfonic acid (Azocarmine B; CI 829). Azocarmine BX is made by the sulfonation of Azocarmine monosulfonic acid with 24% oleum at 70–80°; the dye has poor fastness properties (light 2–3; milling 1–2). Rosinduline GG (CI 830), which has slightly better milling fastness, is made by the fusion of Azocarmine BX with caustic soda under pressure.[4]


Cl
OH
PhNH₂
NHPh
OH
NaOCl
NPh
O
PhNH₂
NPh
PhHN
O
PhNH₂
N
PhHN
N
Ph
Cl⁻
NaO₃S
N
⁻O₃S
HN
SO₃Na
N
Ph
NaOH, 3 atms.,
133–140°, 8 hrs.
NaO₃S
N
O
N
Ph

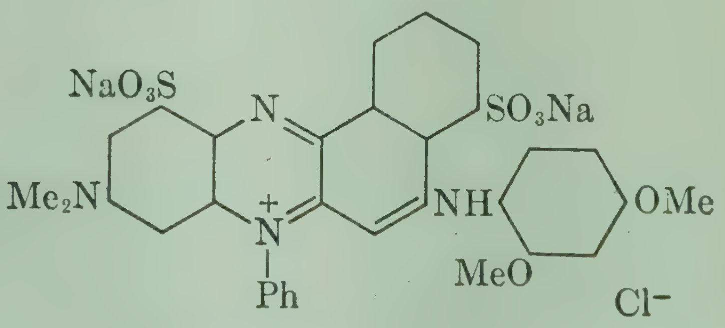
Azocarmine BX

(IV)

Rosinduline GG


N
PhHN
NHPh
N
Ph
Cl⁻

(V)


NaO₃S
N
SO₃Na
Me₂N
NH
OMe
N
Ph
MeO
Cl⁻

Indocyanine 6B

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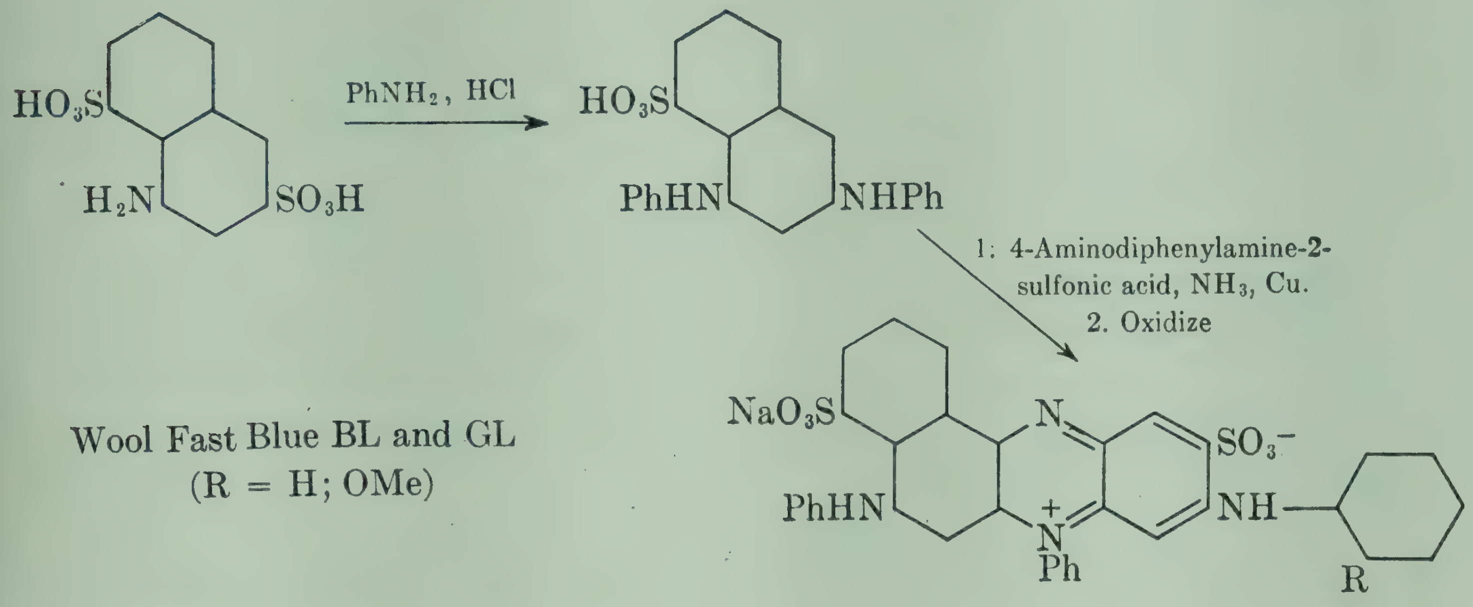
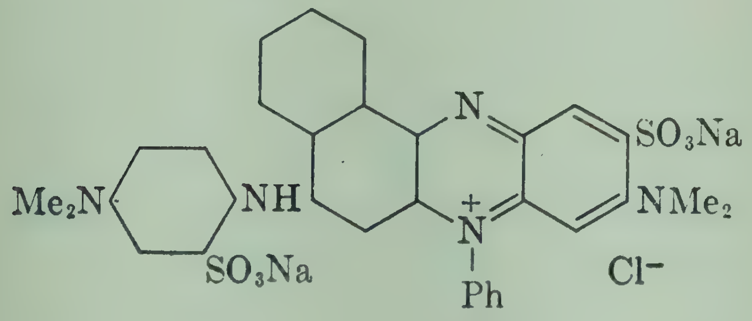
[18] Wahl and Lantz, *Rev. gén. mat. color.* **28,** 33 (1923); St. Denis, DRP 422,119.

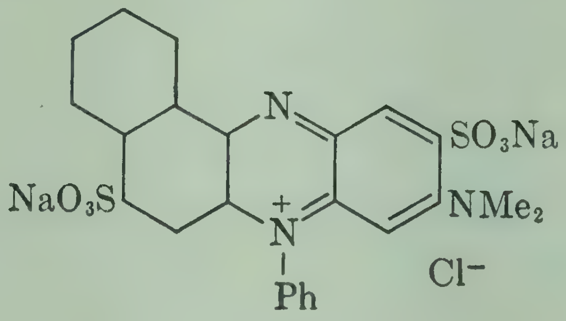
The Milling Blues (K, 1890; CI 856) were obtained by the sulfonation of *N*-arylnaphthosafranines such as (V), which can be prepared by heating benzeneazo-α-naphthylamine, α-naphthylamine hydrochloride and aniline. Examples of faster dyes of the azine series are Indocyanine 6B (AGFA)[6] and Wool Fast Blue BL and GL (Ott, 1907) (By; CI 833), prepared by the indicated series of reactions. The Wool Fast Blues have light fastness 4–5 and milling fastness 3–4. Some of the Polar Blues (Gy) are analogous compounds (e.g. VI).[19] They may be prepared by heating the sulfonic acid (VII), prepared by standard methods, with 4-aminodimethylaniline-3-sulfonic acid; it has been suggested that this new sulfonic group is responsible for the improved fastness of these dyes.


HO3S
H2N
SO3H
PhNH2, HCl
HO3S
PhHN
NHPh
1. 4-Aminodiphenylamine-2-sulfonic acid, NH3, Cu.
2. Oxidize
NaO3S
PhHN
N
SO3−
NH
+
N
Ph
R

Wool Fast Blue BL and GL
(R = H; OMe)


Me2N
NH
SO3Na
N
SO3Na
NMe2
+
N
Ph
Cl−

(VI)


NaO3S
N
SO3Na
NMe2
+
N
Ph
Cl−

(VII)

In preparing acid colors of the azine series, sulfonation at the final stage sometimes offers difficulty. IG claim[20] that sulfonation is rendered more facile by having alkyl groups in the ring A in a dye of the formula (VIII). Supramine Blue EG (IG), prepared by the indicated series of reactions, illustrates this device;[4] it is a level-dyeing acid color with good light fastness. When the dye (IX) is benzylated, a clearer blue shade

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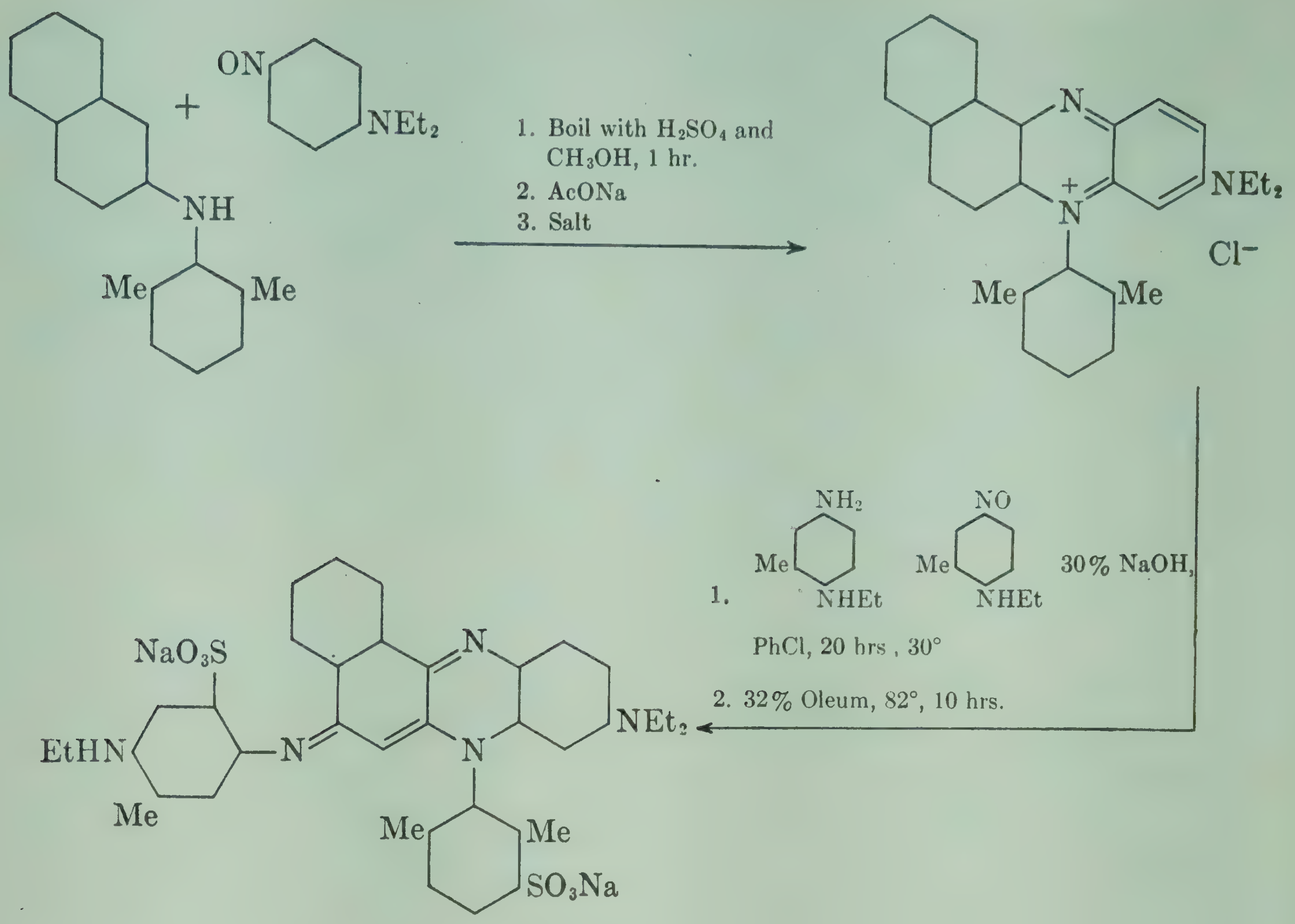
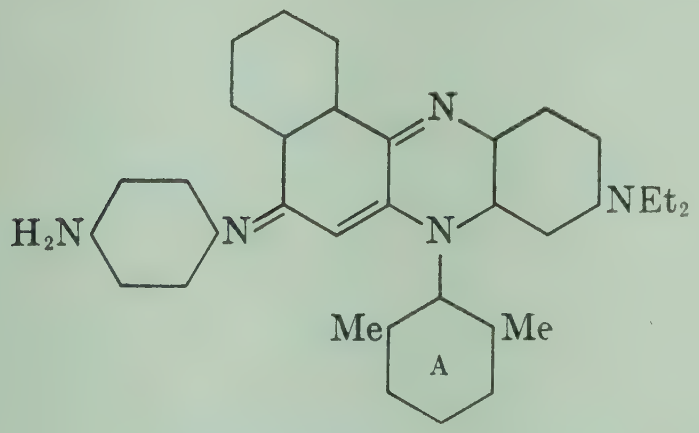
[19] DRP 504,331.

[20] IG, BP 457,448.

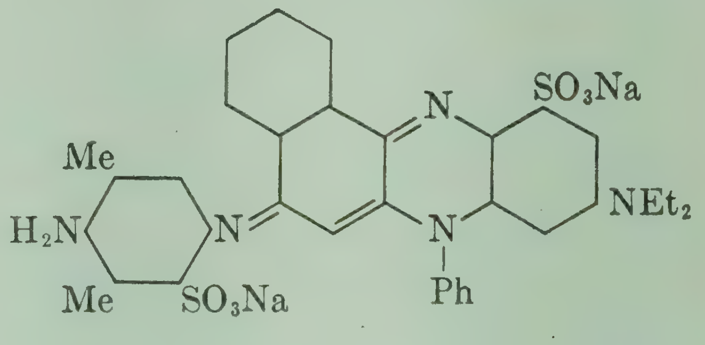

ON
NEt₂
NH
Me
Me
1. Boil with H₂SO₄ and CH₃OH, 1 hr.
2. AcONa
3. Salt
N
N
NEt₂
Cl⁻
Me
Me
1. NH₂ Me NHEt NO Me NHEt 30% NaOH, PhCl, 20 hrs, 30°
2. 32% Oleum, 82°, 10 hrs.
NaO₃S
EtHN
N
N
N
NEt₂
Me
Me
Me
SO₃Na

Supramine Blue EG

and improved fastness to sea water are produced.[21] An ICI patent[22] introduces higher alkyl groups into this type of dyestuff by synthesizing dyes from, for instance, 1,3-dianilinonaphthalene-8-sulfonic acid and a


H₂N
N
N
N
NEt₂
Me
Me
A

(VIII)


Me
H₂N
Me
N
SO₃Na
N
N
Ph
SO₃Na
NEt₂

(IX)

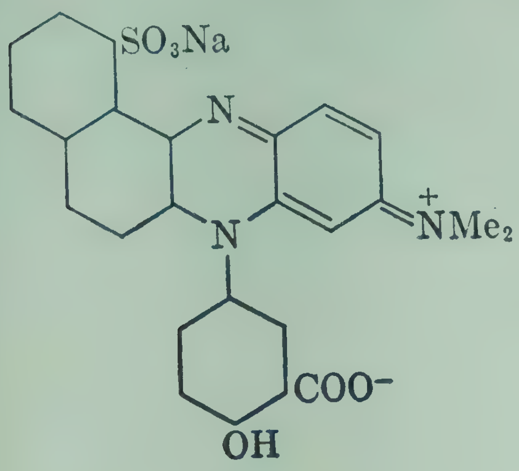
4-amino-4′-alkyldiphenylamine-2-sulfonic acid. By treating two moles of an aminosalicylic acid with one mole of a naphthol-, naphthylamine-, or aminonaphtholsulfonic acid in presence of bisulfite, condensation products having one loosely bound molecule of aminosalicylic acid are obtained.[23] This aminosalicylic acid molecule is easily split off, and by condensation with a nitroso secondary or tertiary aromatic amine,

[21] IG, BP 461,267.

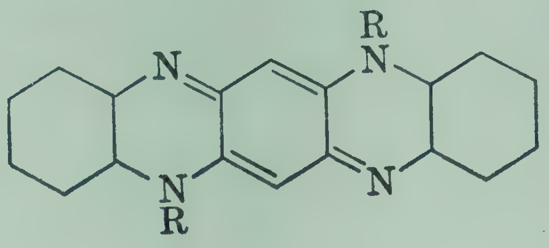
[22] ICI, BP 455,693.

[23] Durand and Huguenin, BP 437,798.

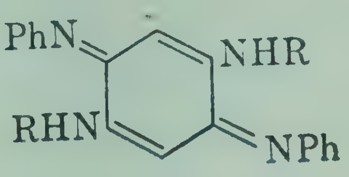
mordant azine dyestuffs of the type (X) are produced. Such dyes are suitable for chrome printing on cotton and give bluish violet to reddish violet shades of good fastness.[24] Fluorindine dyes (XI) are obtained by treating an azophenine of the type (XII) with oxidizing agents such as lead peroxide, pyrolusite or potassium permanganate. The dyes are very sensitive to acids and alkalis, and unsuitable for textile dyeing, but IG claim to have overcome this defect to some extent by building up substituted fluorindines in such a way that they contain either a nitro substituted benzene radical, or a radical of the naphthalene, anthraquinone or pyrene series.[25] These sulfonated diarylfluorindine dyes are of interest for their property of dyeing cotton and viscose directly in blue to green shades, and they represent a new series of substantive dyes.[26]



(X)



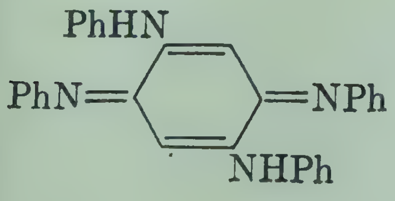
(XI)



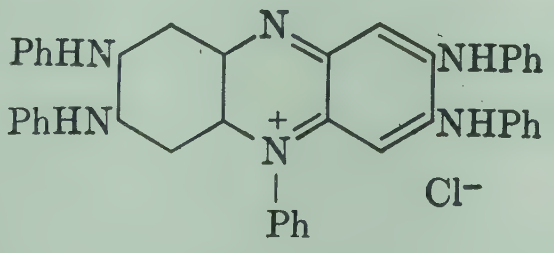
(XII)

Indulines and Nigrosines

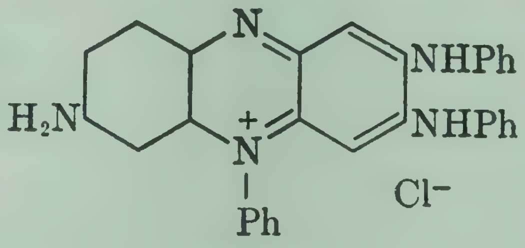
Indulines are blue dyes obtained by heating azo compounds, particularly aminoazobenzene, with aniline and aniline hydrochloride at 180° (Dale and Caro, 1863; Coupier, 1867).[27] Concentrated aqueous solutions can be used, and the blueness of the shade is then controllable by the time of heating; longer heating gives progressively bluer shades. The complex mixtures of azines which are thus formed are insoluble in water, but soluble in alcohol. The initial product is Azophenine (dianilinoquinone dianil), dark red crystals, m.p. 240°. By continued heating



Azophenine



Induline 6B



Induline B

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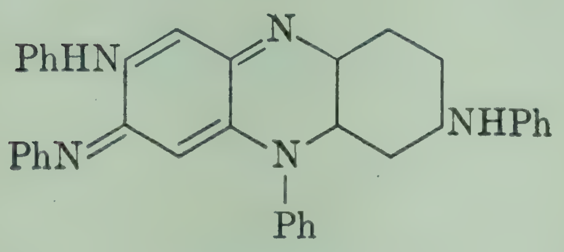
[24] BP 452,346.

[25] BP 442,732.

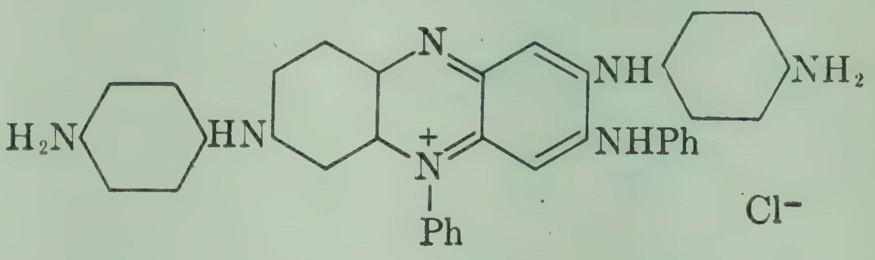
[26] IG, BP 452,006.

[27] Mason in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. VI, Longmans, London, p. 467.

with repeated additions of aniline, condensation and oxidation take place and the ultimate product is Induline 6B. If redder shades are desired (e.g., Induline B and 3B), alcoholic solutions and shorter heating are employed. It is difficult to carry out the reaction in such a manner that the product is a single substance, and the commercial Indulines (CI 859–863) are largely mixtures which are standardized by colorimetric tests. The Indulines may be used as the bases, e.g. Fast Blue Base RF (Induline Base 5BM), which is prepared by heating aminoazobenzene with ferrous chloride and nitrobenzene at 180° for a few hours, and basifying with caustic soda.[4] If a diamine is used in the reaction mixture, or if the spirit-soluble Indulines are heated with p-diamines such as p-phenylenediamine and p-toluylenediamine, more basic products forming water-soluble hydrochlorides are obtained (Indophenine, By; Toluylene Blue, GrE; CI 863). Sulfonation of the spirit-soluble Indulines yields water-soluble Indulines, which are acid dyes (Fast Blue, Solid Blue).

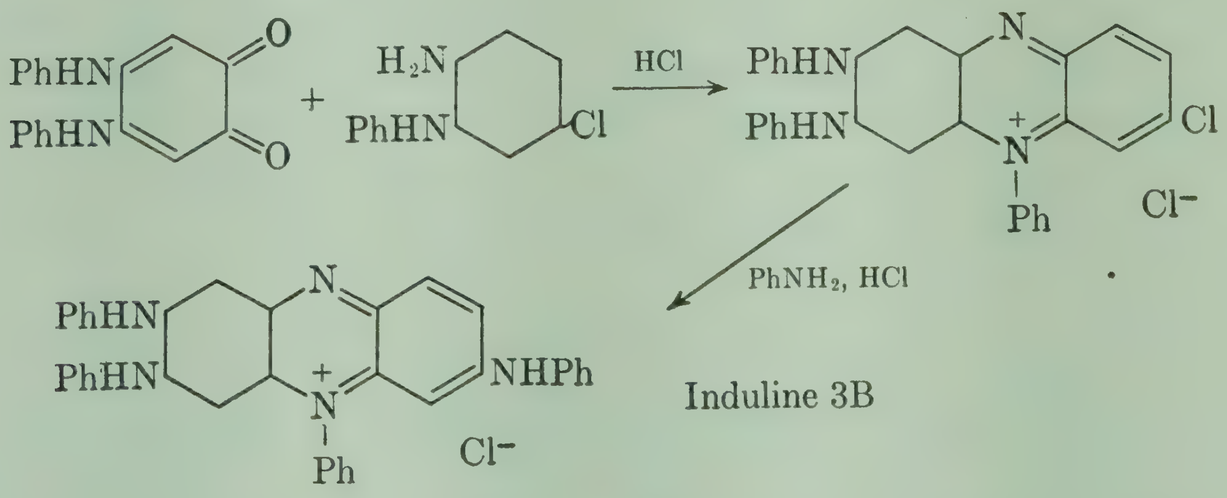


Fast Blue Base RF



Indophenine

The constitution of the main components of the Induline melt has been elucidated by Kehrmann, who synthesized Induline 3B as indicated.[28] Induline 3B was converted into 6B by heating with aniline, aniline salt and mercuric oxide.



Induline 3B

Indulines are formed as by-products in the Magenta melt and in various other reactions of amines and azo compounds, such as the condensation of aminoazo compounds with phenols or quinones and of hydroxyazo compounds with arylamines. The interaction of aminoazobenzenes or of the spirit-soluble Indulines with benzidine hydrochloride leads to direct cotton dyes which have not found practical application.

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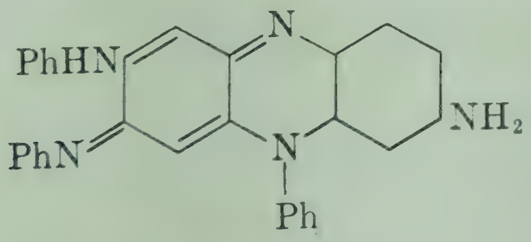
[28] *Helv. Chim. Acta* **8,** 661 (1925).

Nigrosines are black dyes, obtained by heating nitro compounds, such as nitrobenzene or nitrophenols, with aniline and aniline hydrochloride in presence of iron or ferric chloride. Bluer or greener shades, corresponding to the degree of phenylation, are obtained by altering the proportions of reactants and the time of heating. The melt is finally cooled, made alkaline, excess aniline removed by heating in a vacuum pan dryer, and the residual base rendered soluble in alcohol by reprecipitation from an acid solution if necessary; the products are Spirit Nigrosines. Another method of making a Nigrosine (Nigrosine Base CF New, IG) is to heat aminoazobenzene and hydrochloric acid to dryness, and cook at 130–135° for a few hours. Careful control of time and temperature are necessary, since longer cooking and higher temperatures give bluer melts. The melt is made alkaline with aqueous caustic soda; the base is separated and steam-distilled until the aniline content is less than 2%. The low aniline content is necessary for Leather Black Brands, and also because the base becomes sticky and difficult to crush with a higher aniline content. These products, like the Indulines, are mixtures of azines, but usually more complex in character; they are insoluble in water, soluble in alcohol, and convertible into soluble Nigrosines by sulfonation. An example of a simple Nigrosine is Nigrosine C New. The names Induline and Nigrosine are used interchangeably; e.g., Induline Base RM is practically identical with Nigrosine Base CF New, and Induline Base NF is a mixture of Nigrosine Base C and Fast Blue Base R.[4]



Nigrosine C New

The main use of Indulines and Nigrosines is for coloring waxes, boot polishes and printing inks, requiring cheap dyes soluble in oil bases. The spirit-soluble Indulines and Nigrosines are used for staining wood and coloring lacquers. Indulines dissolved in acetin (Acetin Blue) have been used in calico printing, and the Indulines yield shades of moderate fastness as basic dyes on silk and tannin-mordanted cotton. The water-soluble derivatives find some use in dyeing, especially leather dyeing. The annual production of Nigrosines in the United States is over four million pounds.

The Nigrosine and Induline type of dye is improved in the direction of making the unsulfonated dye more soluble in lacquer solvents, such as butyl alcohol, or in plasticizers, by using *p*-anisidine, *p*-phenetidine, or alkoxydiphenylamine in the manufacture in place of aniline or diphenylamine,[29] or by heating the ordinary spirit-soluble Nigrosine or Induline with *p*-phenetidine.[30]

ANILINE BLACK

Discovered by Lightfoot (1860–1863), the Aniline Black process of oxidizing aniline oil on the fiber has remained a very important method for the production of deep fast blacks on cotton, especially in calico printing. It is also prepared in substance for use as a pigment. In its fastness to light and chlorine, Aniline Black is comparable to the much more expensive vat blacks; Sulfur Black is easier to apply, is cheaper than Aniline Black and is equally fast to light; but Sulfur Black has the serious disadvantage of very poor fastness to chlorine and the danger of tendering on storage. The drawbacks of Aniline Black are the need for special plant, the care required in handling the process, and the fact that under the conditions of acid oxidation some tendering of the fiber is inevitable. By skilful control, however, the tendering may be minimized; and unlike Sulfur Black in which the dyeing process is completely innocuous, but progressive deterioration of the fiber can take place months later, any degradation of cellulose occurs during dyeing and may be immediately detected. Since an insoluble coloring matter is formed on the fiber, as in azoic dyeing, good fastness to rubbing can only be obtained under the right conditions of dyeing and aftertreatment. Some Aniline Blacks turn green on exposure to a reducing atmosphere (e.g., sulfur dioxide); this is due to incomplete oxidation, and "ungreenable blacks" can be produced by ensuring that the oxidation proceeds to completion. On the other hand, over-oxidation leads to bronziness in the black shades, apart from the danger of damage to the fiber.

Based on the common principle of oxidizing aniline to a complex azine by means of an oxidizing agent, mineral acid and an oxygen carrier, numerous processes for dyeing and printing Aniline Black are available, and these may be classified in accordance with the oxidation catalyst employed (e.g., vanadium black) or the treatment (dyed, aged, and steam blacks).

Aniline Black is applied by three main processes, of which there are various minor modifications. (1) The simplest, but least satisfactory since the blacks are greenable and the fastness to chlorine and to rubbing is poor, is the single-bath process, used for yarn dyeing ("dyed blacks"). To a solution of dichromate, a solution of aniline, hydrochloric acid and sulfuric acid is added immediately before the dyeing is to commence; copper sulfate or iron acetate may also be added. After working in the cold, the temperature is raised to about 70° (or to the boil if redder shades are required); the yarn is then washed free from acid and soaped. (2) The "aged black" process is the most important for cotton dyeing, and gives the maximum all-round fastness. The dyebath consists of aniline oil, aniline hydrochloride, sodium chlorate, ammonium chloride (as an acid-producing agent), aluminum acetate, and a copper or vanadium salt as oxygen carrier. An essential feature of the process is that wooden or earthenware vessels must be employed. Piece goods are impregnated in a padding machine; the cloth is then dried and given a short passage through an ager at 60–70° when oxidation takes place by the action of hot humid air. The cloth is chromed, if necessary for completing the oxidation, and soaped. (3) The "steam black" or "prussiate black" process is used for calico printing. The usual oxidizing agent is sodium chlorate with potassium ferrocyanide as oxygen carrier. The dyed or printed material is dried and steamed in a rapid ager for a few minutes. Afterchroming is necessary to complete the oxidation.

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[29] Geigy, BP 467,085.
[30] Geigy, BP 467,093.

The addition of *p*-aminodiphenylamine (MLB, 1892) or small amounts of *p*-phenylenediamine or *p*-aminophenol (Green, 1908) is a device for producing ungreenable blacks; in Green's process the padding liquor does not contain an oxidizing agent, air-oxidation during ageing and afterchroming being sufficient for complete oxidation. These modifications however are no longer in vogue.

Aniline Black and similar blacks prepared in substance are useful as pigments. Pigment Black extra (IG) is prepared by oxidizing aniline and crude xylidine in hydrochloric acid solution with sodium dichromate in presence of copper sulfate. The pigment contains chromium and copper; after removal of the metals by means of dilute sulfuric acid, the product is marketed as Pigment Black conc. Other brands are made by using aniline alone, aniline in admixture with *o*-toluidine, etc.[3]

The chemistry of Aniline Black has been examined by Willstätter[31] and Green.[32] There are three distinct stages in the oxidation of aniline: (1) formation of the green Emeraldine, which is the hydrochloride of a blue amine; (2) conversion of Emeraldine to the blue Nigraniline, which can revert to the green Emeraldine by reduction; and (3) final oxidation of Nigraniline to an ungreenable black:

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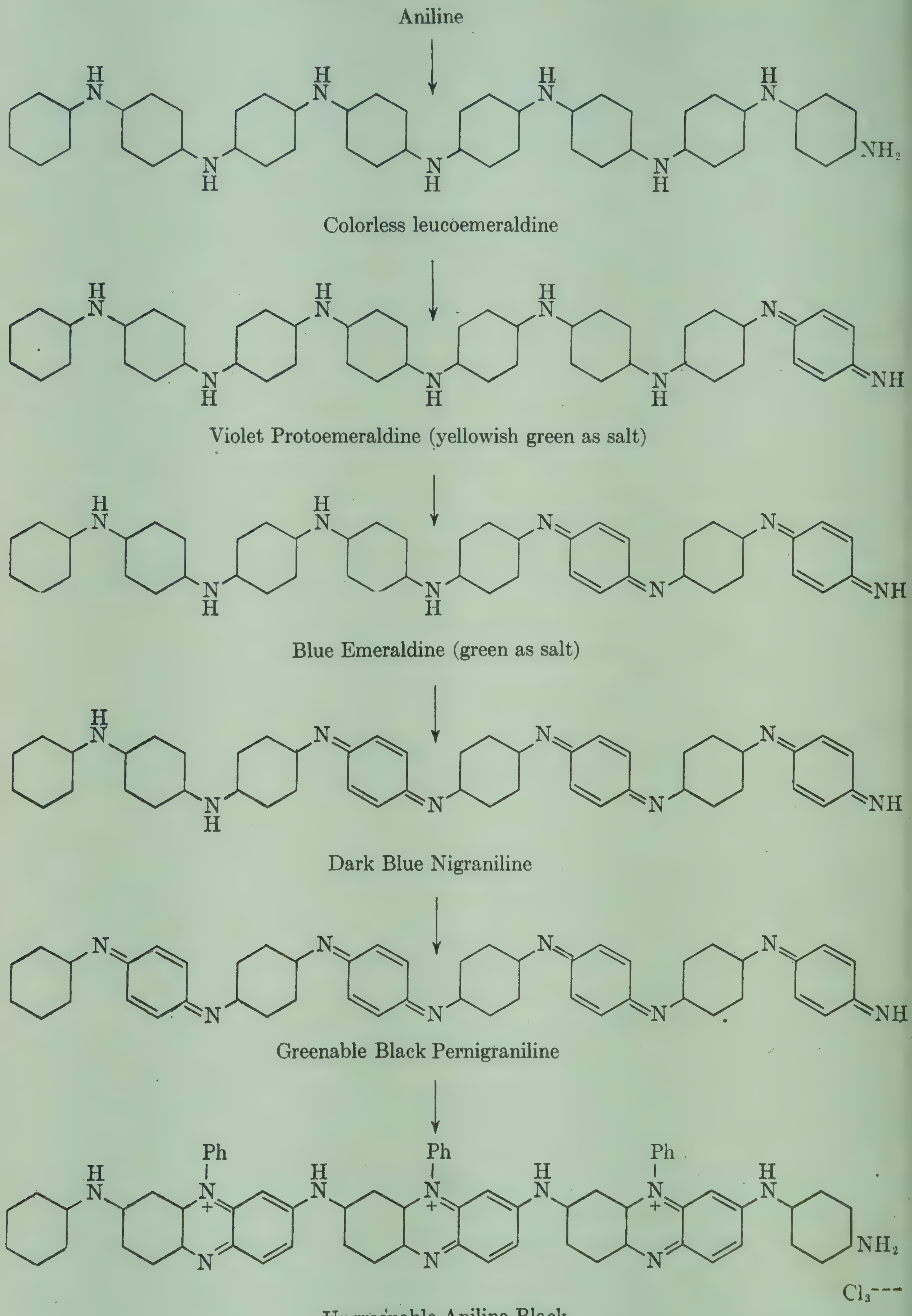
[31] Willstätter *et al.*, *Ber.* **40,** 2665 (1907); **42,** 2147, 4118 (1909).

[32] Green *et al.*, *J. Soc. Dyers Colourists* **29,** 105 (1913).



Aniline

Colorless leucoemeraldine

Violet Protoemeraldine (yellowish green as salt)

Blue Emeraldine (green as salt)

Dark Blue Nigraniline

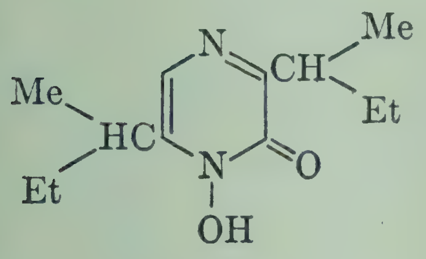
Greenable Black Pernigraniline

Ungreenable Aniline Black

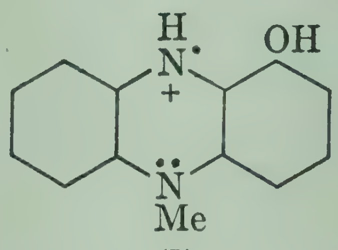
Elementary analysis of Aniline Black corresponds to the empirical formula $(C_6H_5N)_x$, and vigorous reduction yields 4,4′-diaminodiphenylamine. Willstätter found that Pernigraniline or greenable black (one mole) can be oxidized to quinone (7 moles), and hydrolyzed by acid to ammonia (one mole), thus confirming the proposed polyindamine structure and the chain length. The monosubstituted benzene ring at one end of the chain is not oxidized to quinone under the conditions employed. Green supported his structure for ungreenable Aniline Black by showing that it can be obtained from Pernigraniline, prepared in the cold, by further treatment with aniline salt and chromic acid; using *p*-bromoaniline, it was also shown that the conversion of Pernigraniline to Aniline Black involves the addition of three aniline residues.

Naturally Occurring Azines

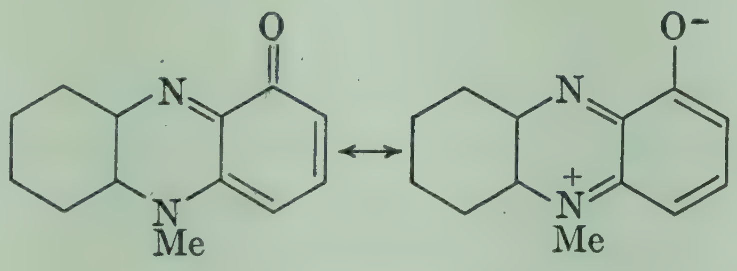
The bright yellow *Aspergillic acid*, an antibiotic produced by the mold *Aspergillus flavus*, is a 1-hydroxy-3,6-dialkyl-2-pyrazone.[33] Among the pigments produced by bacteria are azine derivatives, such as the blue Pyocyanine, a product of *Bacillus pyocyaneus;* it has been shown from the paramagnetism of the perchlorate and other properties that the leuco derivative exists in aqueous solution as the semiquinone ion (I).[34] Pyocyanine has been synthesized from pyrogallol monomethyl ether and *o*-phenylenediamine.[35] Chlororaphine, the green pigment of *Bacillus chlororaphis*, has a quinhydrone structure, being formed synthetically by the addition of phenazine-α-carboxylamide to dihydrophenazine-α-carboxylamide.[36] *Iodinin*, the purple pigment of *Chromobacterium*



Aspergillic acid



(I)



Pyocyanine

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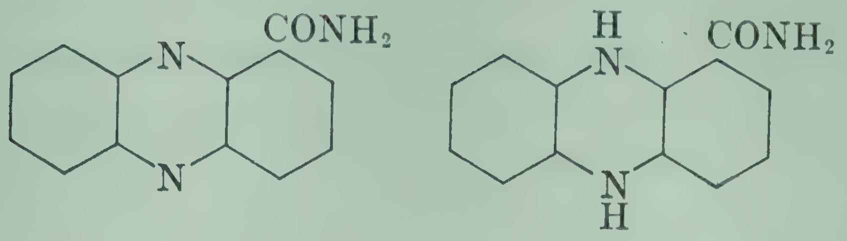
[33] Dutcher and Wintersteiner, *J. Biol. Chem.* **155,** 359 (1944).

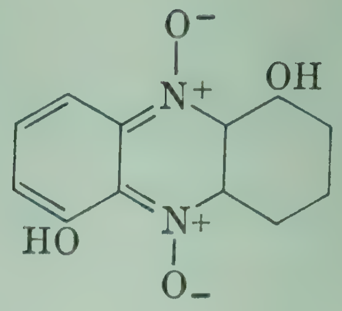
[34] Kuhn and Schön, *Ber.* **68,** 1537 (1935).

[35] Surrey, *Org. Syntheses* **26,** 86; Wrede and Strack, *Ber.* **62,** 2053 (1929).

[36] Kögl *et al., Ann.* **497,** 265 (1932).


CONH₂
H
CONH₂
N
N
H

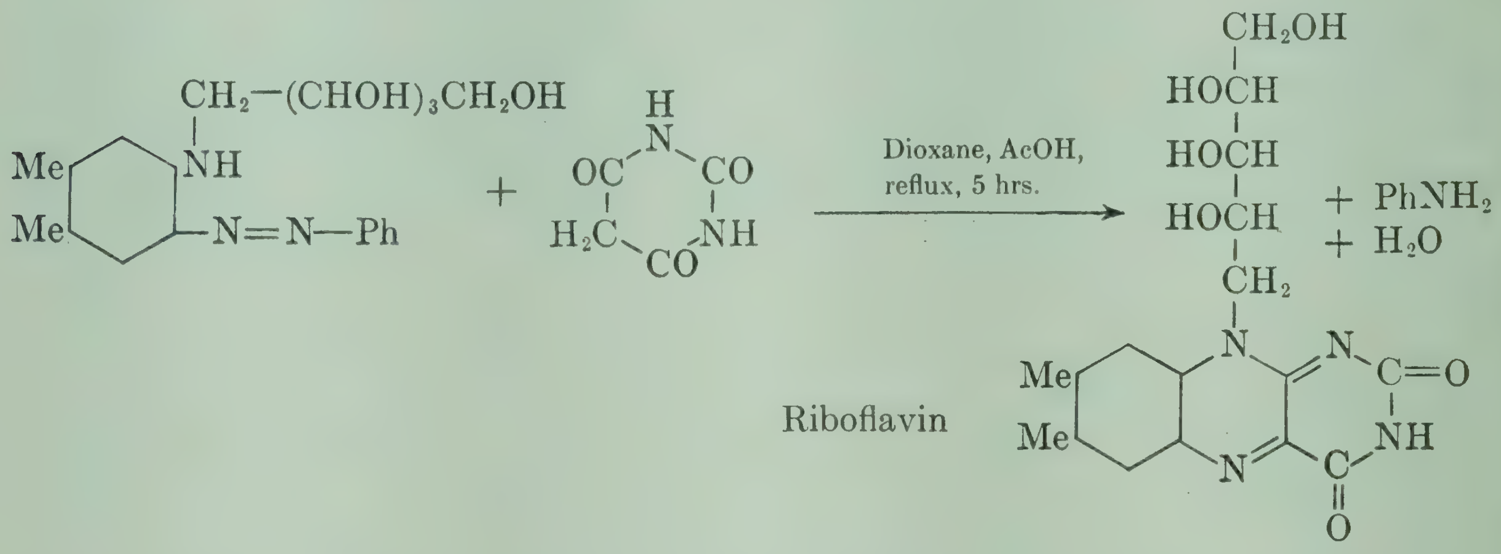
Chlororaphine



Iodinin

iodinum, is the bis-*N*-oxide of a dihydroxyphenazine; it resembles Alizarin in its absorption spectrum, but chemical evidence indicates that the two hydroxyl groups are in the 1,6-positions.[37]

Riboflavin (vitamin B_2) is a quinoxaline derivative, and is typical of the water-soluble, fluorescent yellow pigments (lyochromes) occurring in green leaves, milk and other natural products. It can be synthesized by a method similar to one of the general azine syntheses (cf. Induline Scarlet). 4-Ribitylamino-5-benzeneazo-*o*-xylene reacts with barbituric acid, undergoing reduction to the *o*-phenylene diamine derivative, while barbituric acid is oxidized to alloxan, and the two products then condense to form Riboflavin.[38]


CH₂—(CHOH)₃CH₂OH
NH
Me
Me
N=N—Ph
+
H
N
OC
CO
H₂C
NH
CO
Dioxane, AcOH,
reflux, 5 hrs.
CH₂OH
HOCH
HOCH
HOCH
CH₂
+ PhNH₂
+ H₂O
Me
Me
N
N
C=O
NH
N
C
O
Riboflavin

Oxazines

The oxazines[39] belong to three dyeing classes: basic, chrome mordant and direct cotton colors. The shades are mainly blue. The basic dyes of the series are useful in calico printing for colored discharges on azo dye grounds, since the oxazines are reduced by alkaline hydrosulfite to leuco compounds from which the dyes are regenerated by oxidation. Oxazine dyes are destroyed by oxidizing agents such as chlorates, and can therefore be used for white discharge effects. The chrome mordant dyes (Gallocyanine class), which are valuable for both cotton and wool, and the light-fast direct cotton dyes (some of the Sirius Supra Blues and Violets) are much more important than the basic oxazines.

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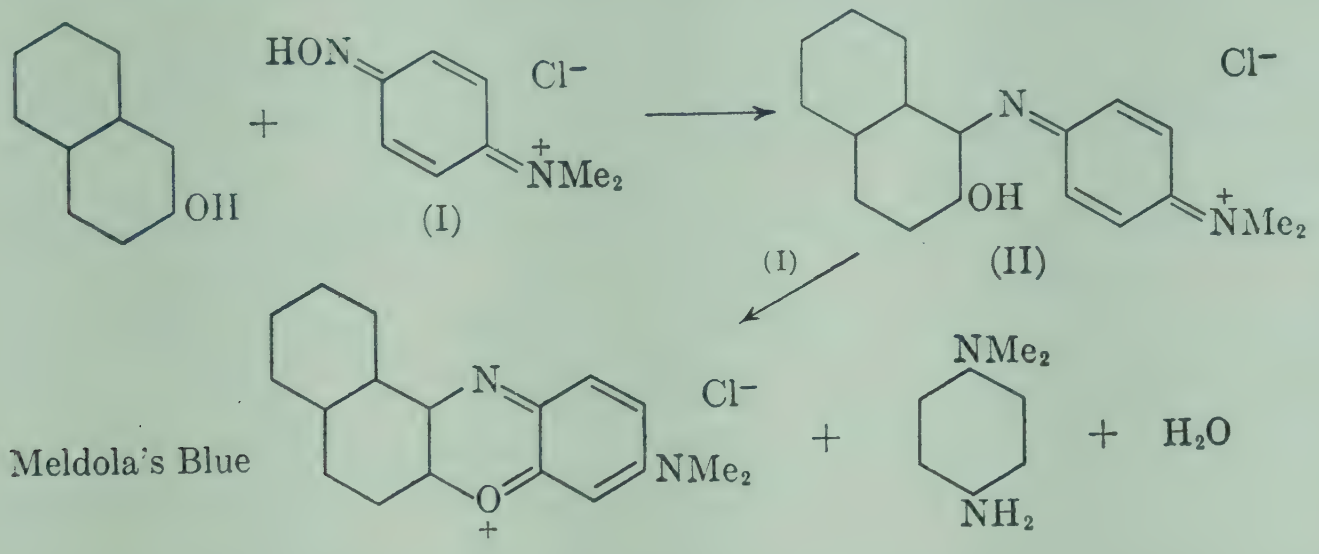
[37] Clemo and McIlwain, *JCS* 479 (**1938**); McIlwain, *ibid.* 322 (**1943**); Clemo and Daglish, *JCS* 1481 (**1950**).

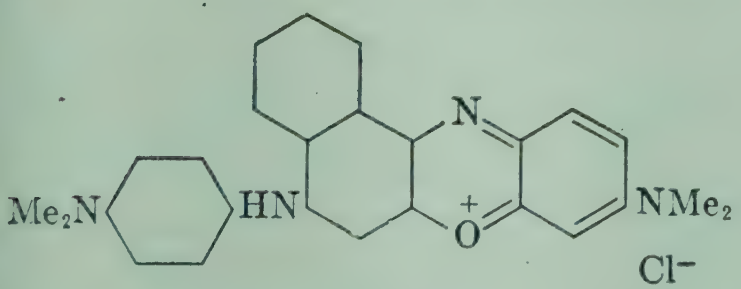
[38] Tishler *et al.*, *JACS* **69,** 1487 (1947); see also Bergel, Cohen and Wynne, BP 550,836.

[39] See Coffey in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. IX, Longmans, London, p. 149.

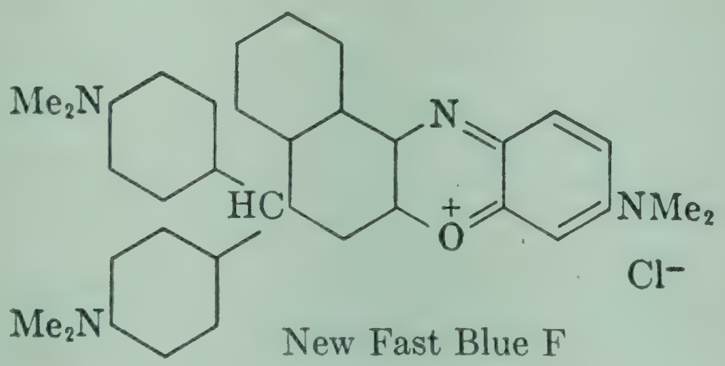
Meldola (1879) discovered the first oxazine dye, Meldola's Blue, prepared by heating β-naphthol (2 moles) with excess of *p*-nitrosodimethylaniline hydrochloride (I) (3 moles); the third mole acts as oxidizing agent for converting the intermediate indophenol (II) into the oxazine.



p-Aminodimethylaniline is a recoverable by-product. Oxidation may be accelerated and the yield improved by blowing air through the reaction mixture. The zinc chloride double salt is prepared by adding a mixture of nitrosodimethylaniline hydrochloride, zinc chloride and alcohol to an alcoholic solution of β-naphthol under carefully controlled conditions, and keeping at the boil for a few minutes.[4] Meldola's Blue (CI 909) (New Blue R) (Fast New Blue 3R, IG, which is the zinc chloride double salt) was valued at one time as a substitute for indigo in dyeing and calico printing, and as a cheap, bright basic dye for topping vat blues; but it has little interest now for such purposes because of the poor fastness of the shades to light and alkali. It is still largely used, however, for dyeing leather, and to a limited extent in calico printing for discharge effects. The dry dyestuff attacks the mucous membrane. Meldola's Blue condenses readily with bases such as *p*-aminodimethylaniline in the 4-position of the naphthalene residue; thus when a larger excess of (I) is employed in the Meldola's Blue synthesis under more prolonged conditions of

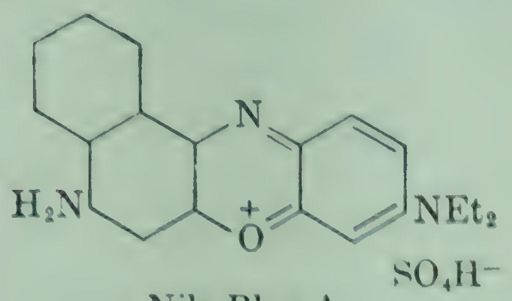


New Blue B

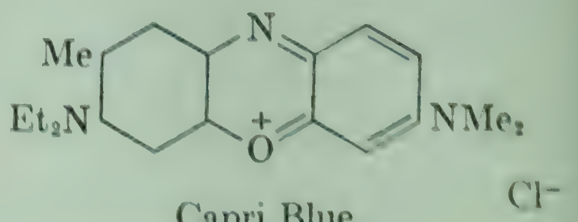


New Fast Blue F

treatment, the product is New Blue B (CI 910), which dyes a bluer shade than Meldola's Blue and is faster to light. Dimethylamine reacts similarly with Meldola's Blue, yielding New Methylene Blue GG (CI 911). Meldola's Blue can also condense with secondary alcohols; with Michler's hydrol the product is New Fast Blue F. These interesting reactions have not led to commercially valuable dyes. Nile Blue A, made by condensing α-naphthylamine with 3-hydroxy-4-nitrosodiethylaniline, is useful as a microscopic stain; the amino group is readily hydrolyzable and as a result of the formation of a phenoxazone neutral fat is stained red while nitrogenous matter is stained blue. The analogs from *N*-ethyl- and *N*-benzyl-α-naphthylamine are Nile Blue BX[9] and Nile Blue 2B (CI 914). These basic dyes are of some interest in dyeing and printing for the brightness of the shades. By partial hydrolysis of such naphthophenoxazines, other dyes have been prepared for special use as stains in cytological work. Certain oxazines (e.g., Nile Blue 2B) stain and inhibit the growth of cancer cells.[39a]



Nile Blue A



Capri Blue

Blue to black dyes, suitable for dyeing cellulose acetate rayon, are obtained by condensing *p*-nitrosodimethyl- or diethylaniline hydrochloride with 1,5-dihydroxynaphthalene in aqueous alcoholic solution containing at least 30% water, preferably with the addition of manganese dioxide as catalyst. The presence of water is essential; otherwise gray dyes are produced.[40]

While the first oxazine dye was a naphthophenoxazine, phenoxazines were made a little later, and some were found to be brighter and faster dyes than the naphthalene derivatives. Phenoxazine (m.p. 156°), the parent compound of the series, can be prepared by heating *o*-aminophenol or its hydrochloride with catechol at 260°.[41] The Capri Blues (Bender, 1890) (L; CI 876), made from *p*-nitrosodialkylanilines and dialkylamino-*p*-cresol, are basic dyes which give brilliant blue shades with moderate fastness to washing; on acetate silk they exhibit good fastness to light. Brilliant Cresyl Blue BB (CI 877), a similar dye used formerly in calico printing for tannin discharge effects and as a cellulose acetate dye, is repared by condensing 2-diethylamino-5-nitroso-*p*-cresol with *p*-phenyl-nediamine. Rhoduline Pure Blue 3G is prepared by nitrosating diethyl-ı-phenetidine, and condensing with *m*-diethylaminophenol. A purer

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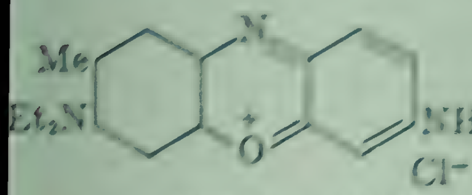
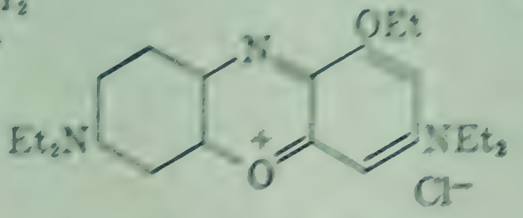
[39a] Sloviter, *JACS* **71,** 3360 (1949).

[40] Bedford, BP 428,143.

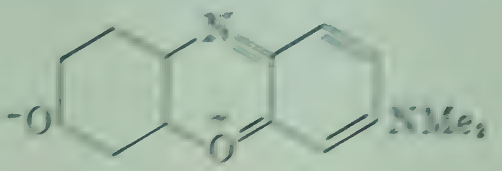
[41] Bernthsen, 1887; Kehrmann and Neil, *Ber.* **47,** 3107 (1914).



Brilliant Cresyl Blue



Rhoduline Pure Blue 3G



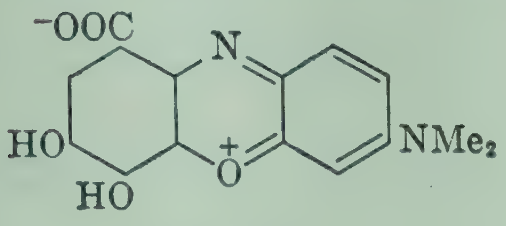
Nitroso Blue

orm of the dye, nearly free from salt, is marketed as Zapon Fast Blue 3G, or coloring lacquer.[4]

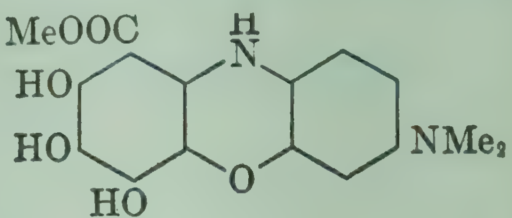
The Meldola reaction proceeds so readily that oxazine dyes may be repared on the fiber. Thus by printing cotton with a thickened mixture f resorcinol, (I), oxalic acid and tannin, and steaming, Nitroso Blue is ormed and simultaneously fixed by the mordanting action of the tannin.

The most important dyes of the oxazine class are the Gallocyanines. Gallocyanine (Koechlin, 1881; CI 883) is made in 95% yield by boiling a nethanol solution of gallic acid and excess of (I); for some reason, which s still not understood, ethanol cannot replace methanol as a solvent for the eaction. Gallocyanine BS is the bisulfite compound. Gallocyanine lyes violet on chrome mordant; since it possesses both basic and mordant lyeing properties, it is best fixed by using a combination of tannic acid nd metallic salts as mordant. Dyes of this type are valuable in calico rinting, and are generally applied in conjunction with tannin and hromium acetate. They are also useful in wool dyeing, although the leep, bright blue shades on chrome mordant have only moderate fastess. For wool dyeing, Gallocyanine may be used as the sulfonic acid f the leuco compound; Gallocyanine MS (CI 885) is obtained by sulfonaion of leucogallocyanine, and Brilliant Gallocyanine (Chromocyanine V; CI 888) by heating Gallocyanine with aqueous sodium bisulfite in an utoclave.

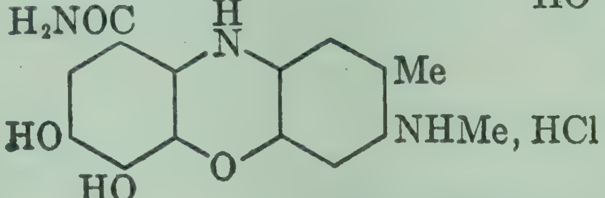
The methyl ester of Gallocyanine, prepared from methyl gallate, is a luish violet dye, Prune, used in printing for chlorate discharges. The allocyanine derivative prepared from gallamide is marketed as the oluble bisulfite compound, Gallamine Blue (DH; CI 894). The gallnilide analog is Gallanil Violet (CI 896). The more soluble leuco comounds are often more convenient to use in calico printing. The Modern DH) colors were specially produced for this purpose, and they are largely sed in calico printing with a chromium mordant, specially for chlorate discharges. Modern Violet (DH) was prepared by reducing Gallamine Blue with sodium sulfide and acid. When steam is passed through a solution of leucogallocyanine and sodium sulfate, the carboxyl group is eliminated, and the hydrochloride, which can be salted out, is Modern Violet N (de la Harpe, 1907; CI 881). Modern Heliotrope DH (CI 882) is prepared by condensing gallamide with 5-nitroso-*N*-methyl-*o*-toluidine, and reducing the product to the leuco compound. Celestine Blue B is made from *p*-nitrosodiethylaniline and gallamide, and Meta Celestine Blue is the homolog from nitrosodiethyl-*m*-toluidine.[4] The Modern Blues (CI 886) are obtained by the action of formaldehyde on Gallocyanines, treatment with water or acid at 100–200°, and reduction to the leuco compounds. Cyanazurine (CI 887) is the reduction product of arylated Gallocyanines. Modern Azurine DH (CI 899) gives bright blue shades on chrome-mordanted fabrics; it is prepared by a complex reaction in which the anilide of Gallocyanine is heated with alcoholic hydrochloric acid and then reduced. If air is blown through a mixture of hot aniline and Gallocyanine hydrochloride, the carboxyl group is replaced by the anilino group, and when the product is sulfonated, the ammonium salt is the acid-mordant wool color, Delphine Blue B (CI 878). It can also be used as a chrome-printing color for cotton. When the aniline condensation is carried out in the cold, the anilino group enters the free position adjacent to the carboxyl group; the carboxyl group may then be removed by heating the product to 100°, and sulfonation with fuming sulfuric acid gives Chromazurine E or G (DH; CI 879). This is a more useful dye than Delphine Blue, giving on chrome-mordanted wool and as a chrome-printing color on cotton bright blue shades similar to Methylene



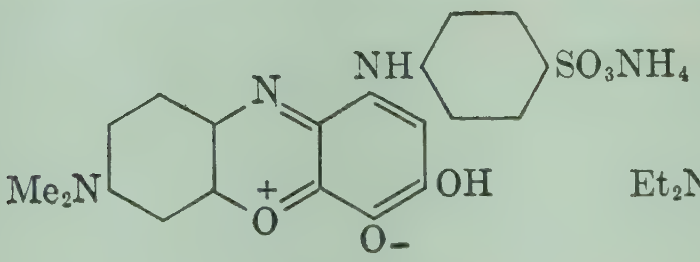
Gallocyanine



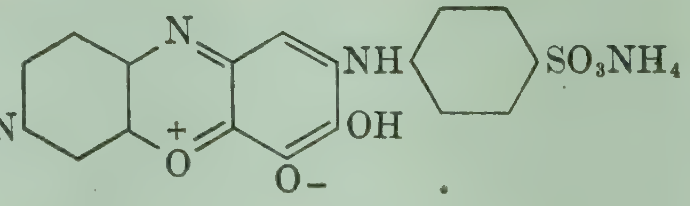
Modern Azurine DH



Modern Heliotrope DH



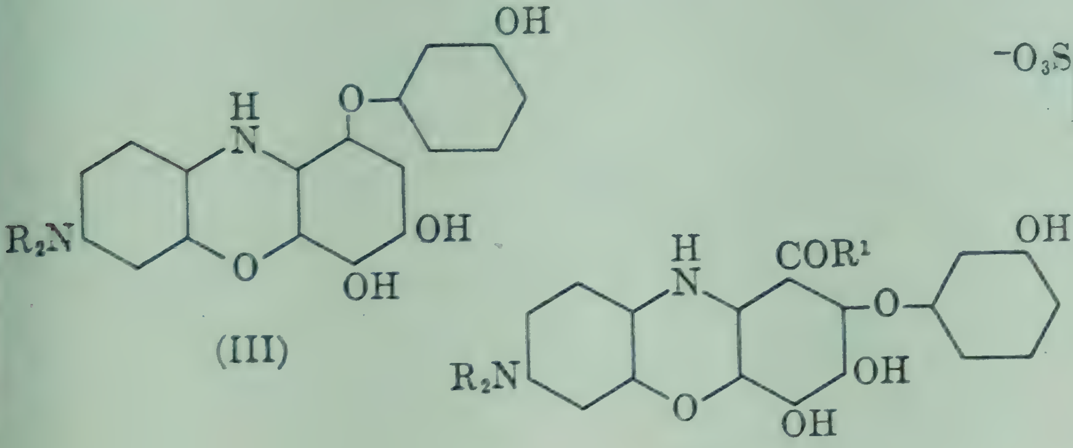
Delphine Blue



Chromazurine E or G

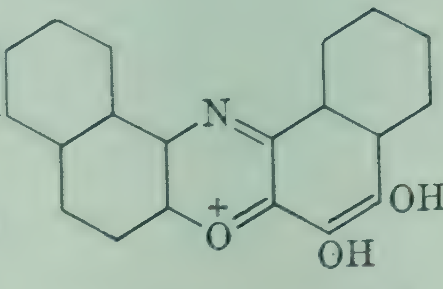
Blue. Gallanil Blue (CI 897) is produced by treating Gallanil Violet with aniline.

Gallocyanine and its derivatives condense with resorcinol, as with aniline, by replacement of the carboxyl group or by attachment to the adjacent position, depending on conditions. The Phenocyanines (III and IV; CI 902), which give indigo-blue shades on a chrome mordant, are prepared by acid condensation, and Ultracyanine B (CI 901) by alkaline condensation.



(III)

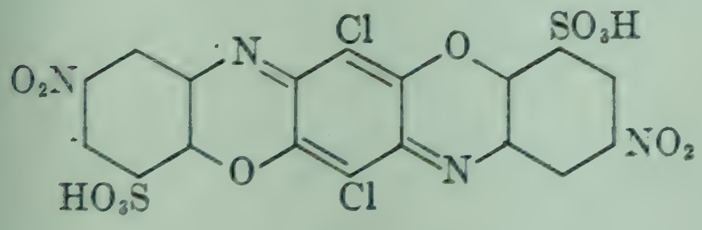
(IV)



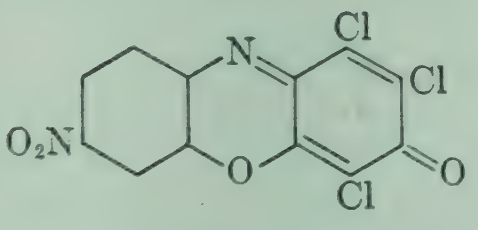
Alizarin Green G

Alizarin Green G (CI 917) dyes bluish green on chrome-mordanted wool, and is prepared by boiling an aqueous alkaline solution of 1,2-naphthoquinone-4-sulfonic acid and 1-amino-2-naphthol-6-sulfonic acid.

Dyes of the Gallocyanine series containing aminoethanesulfonic acid and aminopropanesulfonic acid groups have been patented. These are obtained in the customary manner by condensing, for instance, *p*-nitrosophenylethyltaurine with gallic acid or gallamide,[42] and the dyes are said to be suitable for printing, which is the main use for the Gallocyanine dyes. The diarylaminobenzoquinones obtained by condensing chloranil with amines can be cyclized to oxazines by oxidation; but when derivatives of an *o*-aminophenol are used, ring closure to the oxazine occurs by elimination of water. Normally, *o*-aminophenols will not give oxazines unless they contain nitro groups. If 4-nitro-2-aminophenol-6-sulfonic acid is condensed with chloranil and cyclized in sulfuric acid, the product (V) dyes cotton in brownish orange shades. From 5-nitro-2-aminophenol (1 mole) and chloranil (1 mole), the compound (VI) can be obtained.[43]



(V)



(VI)

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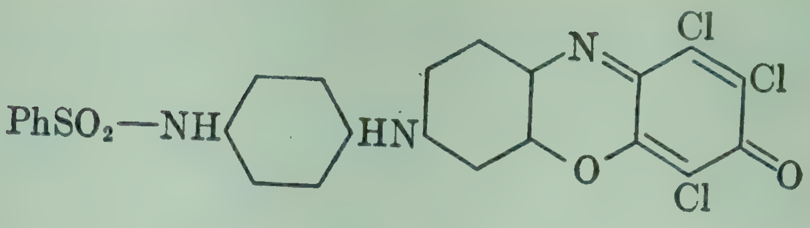
[42] IG, BP 417,875; 436,096.
[43] IG, BP 411,132.



(VII)

The new quinone vat dyes of the type of (VII) containing a sulfonamido group dye reddish to greenish blue, and are said to be particularly suitable for machine dyeing.[44]

o-Alkoxy derivatives of dianilinobenzoquinones cyclize to oxazines by loss of alcohol when heated with benzoyl chloride. Thus dianisidine gives a red dye which, after sulfonation, dyes cotton direct. This method of synthesis is said to give particularly pure products.[45] 1,3-Dinitrophenoxazine (golden orange) and 1,3-dinitrophenothiazine (golden brown) are applicable to cellulose acetate.[45a]

Direct Cotton Colors of the Dioxazine Series

A recent and very important development in the oxazine series (Kränzlein, Greune and Thiele, 1928) is the preparation of direct cotton colors with excellent fastness to light. Brilliant blue dyes, which are dioxazines, are obtained by condensing suitable polycyclic amines with chloranil, and sulfonating the products.[46–48] Thus Sirius Supra Blue FFR or FFRL (formerly Sirius Brilliant Blue RL)[48a] is prepared by the condensation of two moles of 3-amino-*N*-ethyl-carbazole (VIII) with one mole of chloranil, cyclization of the intermediate di-imine (IX) to the dioxazine (Pigment Fast Violet R Base) by means of benzenesulfonyl chloride, and sulfonation to the tri- or disulfonic acid. The dye is the sodium salt. It is necessary to use pure iron-free sulfuric acid for the sulfonation and control the reaction carefully to avoid redder and duller shades. The annual IG production of Sirius Supra Blue FFRL, which has light fastness 7, was 35000 kg.[48] Sirius Light Blue FFGL is also made by the condensation of (VIII) and chloranil, but in pyridine solution. The amine (200 kg.), chloranil (137 kg.) and pyridine (2000 kg.) are stirred for one hour periods at 0°, 15° and 80°. On slow cooling to 20°, the product is filtered, washed and dried at 40–45°. This temperature

[44] IG, BP 399,583.

[45] Brunner and Thiess, BP 416,887.

[45a] Olpin and Law, USP 2,464,885.

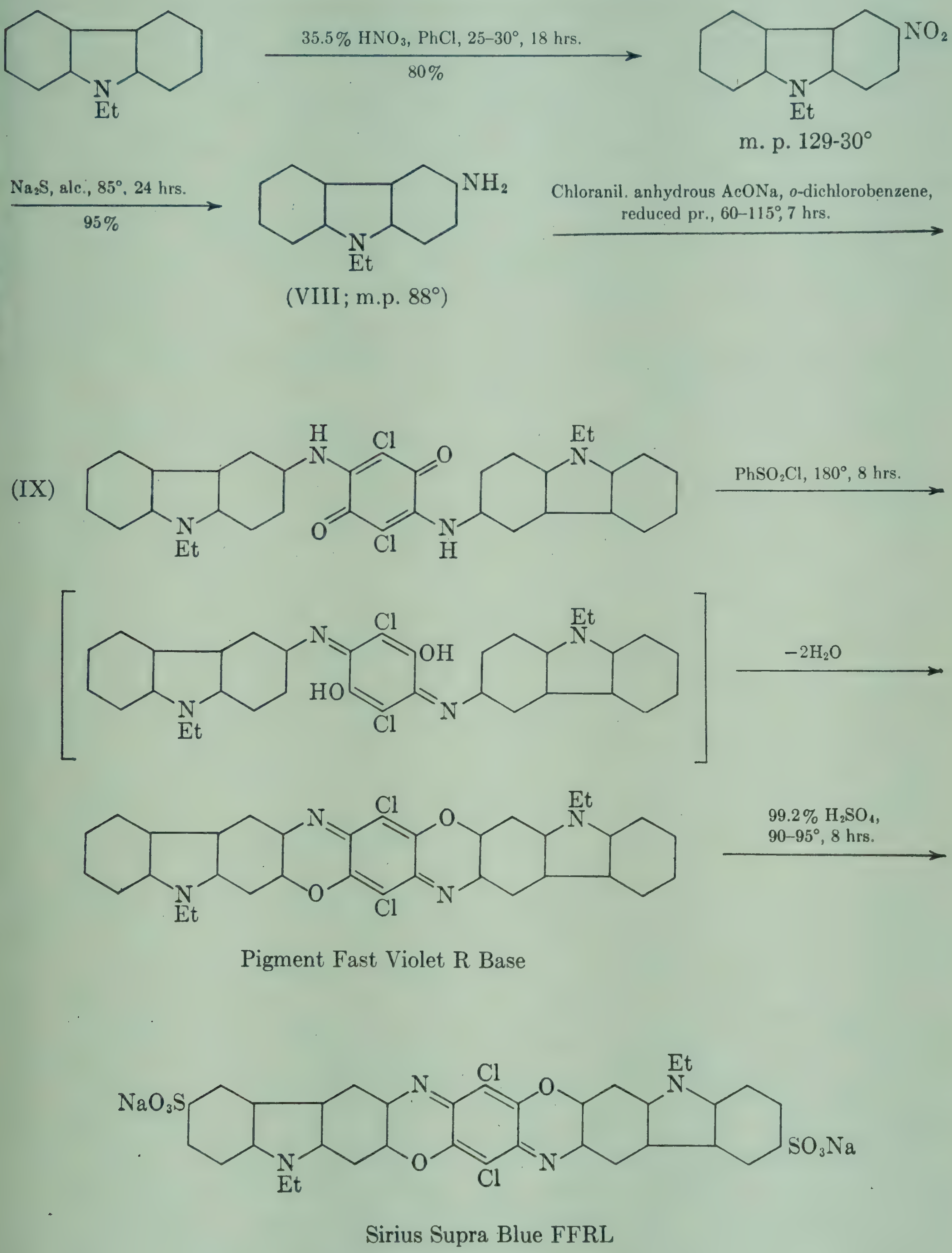
[46] For details of preparation, see *BIOS* **960.**

[47] MLB, BP 8886 (1912); IG, BP 313,094.

[48] *FIAT* **1313** III.

[48a] The Sirius Supra Blues are also known as Sirius Brilliant Blues and Sirius Light Blues.

CHART 1
PREPARATION OF SIRIUS SUPRA BLUE FFRL


N
Et
35.5% HNO₃, PhCl, 25–30°, 18 hrs.
80%
NO₂
N
Et
m. p. 129-30°
Na₂S, alc., 85°, 24 hrs.
95%
NH₂
N
Et
(VIII; m.p. 88°)
Chloranil, anhydrous AcONa, o-dichlorobenzene, reduced pr., 60–115°, 7 hrs.
(IX)
H
N
Cl
O
Et
N
N
Et
O
Cl
N
H
PhSO₂Cl, 180°, 8 hrs.
N
Cl
OH
Et
N
N
Et
HO
Cl
N
−2H₂O
N
Cl
O
Et
N
N
Et
O
Cl
N
99.2% H₂SO₄, 90–95°, 8 hrs.
Pigment Fast Violet R Base
NaO₃S
N
Cl
O
Et
N
N
Et
O
Cl
N
SO₃Na
Sirius Supra Blue FFRL

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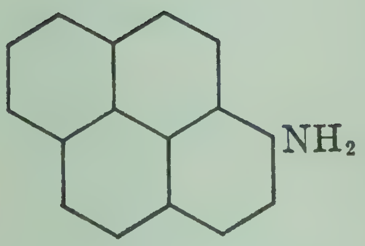
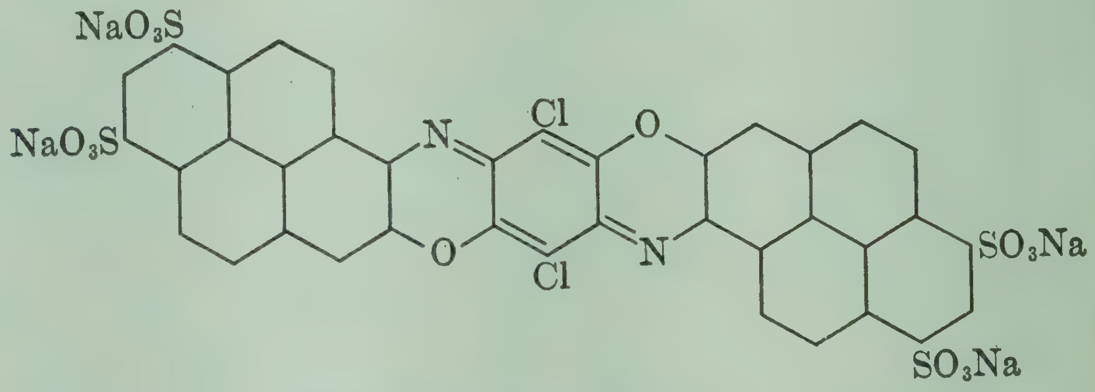
should not be exceeded as the condensate (224 kg.) contains pyridine of crystallization (pyridine content 19–20%) which is necessary for the next stage. Ring closure and sulfonation are simultaneously effected by heating this product with 20 times its weight of 99.8% sulfuric acid at 95–100° for 6–7 hours. After addition to crushed ice, the sulfonic acid is filtered off; the product is washed with brine, dissolved in sodium carbonate solution and salted out. The commercial dye contains 41.5% of the pure color, shaded with Sirius Supra Green BB, and standardized with common salt, sodium acetate and Igepon T. Sirius Light Blue F3RL, the dioxazine dye[49] from 3-aminocarbazole and chloranil, appears to have been superseded by Sirius Light Blue FFRL, the *N*-ethyl derivative. When chloranil is condensed with 3-aminocarbazole in chlorophenol solution and the cyclization is effected in concentrated sulfuric acid, the product is Sirius Brilliant Violet F3BL.

Sirius Light Blue F3GL utilizes 1-aminopyrene (X) and chloranil. Pyrene in the form of a 40% aqueous paste is nitrated with 22% nitric acid (four times the weight of dry pyrene) at 40–45° for 8 hours. The strength of the nitric acid is critical, and all contamination with iron must



(X)



Sirius Light Blue F3GL

be avoided. The yellow-brown nitropyrene, m.p. 148–150°, is reduced to the amine by means of sodium hydrosulfide (about an equal weight) in boiling aqueous ethanol during 7 hours. On diluting and cooling, 1-aminopyrene, m.p. 116–117°, crystallizes out. The condensation of (X) and chloranil is effected in *o*-chlorophenol-ethanol solution in presence of sodium acetate at 0–25° during 20 hours. The product ("Pyranil") is collected, dried at 100°, and purified by reduction with phenylhydrazine in boiling chlorobenzene to the leuco compound, which is filtered off on cooling, and reoxidized to pyranil by heating with nitrobenzene at 190° for about an hour. The fine hair-like crystalline brown substance, m.p. 331–332°, is collected, after steam-distilling the nitrobenzene, dried, and cyclized to "Pyroxazine" by means of *p*-toluenesulfonyl chloride in α-chloronaphthalene at 260°. In view of the danger of decomposition

[49] *BIOS* **1482**.

at this high temperature in a batch process, a special continuous method is employed, with a diphenyl oxide heating bath. The water from the reaction is boiled off continuously. Pyroxazine is then filtered off on a nutsche, dried and sulfonated by treating with about fifteen times its weight of monohydrate at 20° during 36–40 hours. The sodium salt is finally isolated in the usual manner. In the constitution given for Sirius Light Blue F3GL, the positions of the sulfonic groups are the probable ones. A mixture of Sirius Light Blue F3GL and the yellow dye produced by hypochlorite oxidation of 2-*p*-aminophenyl-6-carboxybenzothiazole sulfonic acid is marketed as Sirius Light Green GGL or GG. Sirius Light Violet FFR or FRL is prepared from chloranil and 2-aminofluorene.[48]

Sirius Light Blue FF2GL is the dioxazine dye prepared from 4-aminodiphenylamine-2-sulfonic acid (100 parts) and chloranil (47 parts) heated with magnesium oxide (17.5 parts) at 60° for 6 hours; the base is then sulfonated with 8.3% oleum at 50–55°.[49, 50] Using 4-chloro-4′-aminodiphenylamine-2′-sulfonic acid in this condensation, the product is Sirius Light Blue FFB (formerly FFBL), which dyes useful reddish blue shades (light fastness 5).[48]

The intense activity of IG in the search for new dyes of the dioxazine series is an indication of the potential value of this type. Instead of introducing sulfonic groups into dioxazine dyes by condensing in sulfuric acid or by sulfonating the condensation products, sulfonated primary aromatic amines themselves may be used as starting materials. By condensing sulfonated primary aromatic amines which contain more than two nuclei, e.g., 3-amino-9-ethylcarbazolesulfonic acids, with chloranil in concentrated or fuming sulfuric acid or chlorosulfonic acid in the presence of oxidizing agents, blue oxazine dyes are obtained. The yields are higher than those obtained by simultaneous condensation and sulfonation.[50] Fast blue dyes are produced by condensing aminodiphenylaminesulfonic acids with chloranil.[51]

In a series of patents,[52] IG describe the preparation of dioxazine dyes from diarylamino-*p*-benzoquinones or 2-arylamino-5-alkoxy-*p*-benzoquinones, as well as methods for making these intermediates. Thus halogenated *p*-benzoquinones, an alcohol, and an acid-binding agent yield alkoxy-halogeno-*p*-benzoquinones, one halogen being replaced. These are condensed with ammonia or primary amines, so that one more halogen is replaced, and the products can then be condensed again with a different amine to give unsymmetrical diamino-*p*-benzoquinone derivatives by replacement of the alkoxy group.[53] A large variety of intermediates is mentioned. The dioxazine dyes may also be made from 5-halogeno-2-arylamino-*p*-benzoquinones and an arylamine chosen to give an unsymmetrical diarylamino-*p*-benzoquinone, and the dyes or the intermediates may be sulfonated. Other IG patents in this series relate to the condensation of diamines such as benzidine and diaminodiphenylurea with chloranil, followed by ring closure and sulfonation to give violet dyes having good affinity for cotton.[54] In the preparation of these dyes two moles of diamine are used to one mole of chloranil, so that the dyes are probably sulfonic acids of compounds such as (XI). Since ring closure is effected in presence of benzoyl chloride, they may be benzoyl derivatives. Another variation is to condense chloranil with *p*-phenylenediamine mono- or disulfonic acid (2 moles), or with naphthylenediaminesulfonic acids, and cyclize to blue and gray dyes.[55] By condensing benzoquinone or chloranil with acylated diaminobenzenes, e.g., monoacetyl-*p*-phenylenediamine, bisacylamidoarylaminoquinones are obtained, which are then cyclized to give bluish-gray to violet dioxazines. The unsulfonated products may be used for coloring rubber or may be converted into water-soluble dyes by sulfonation.[56]

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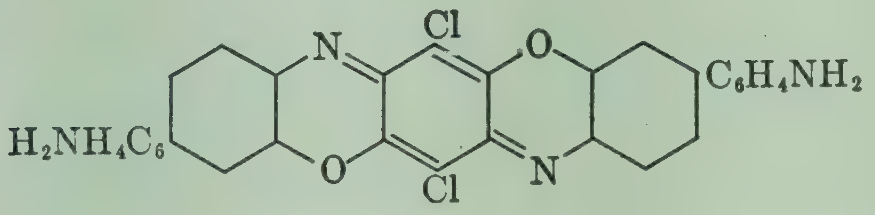
[50] IG, BP 447,899.

[51] IG, BP 448,182.

[52] IG, BP 509,890–1; 509,893; 509,898.



(XI)

Dioxazine dyes containing azo groups are obtained by condensing *p*-benzoquinone or chloranil with an aminoazo compound and sulfonating. The shades vary from bluish-green to violet and the dyes are stated to be distinguished by their affinity for vegetable fibers and good fastness properties. As suitable aminoazo compounds, aminoazobenzene, aminoazonaphthalene, and benzeneazoaminocarbazole are mentioned.[57]

When *N*-benzoyl and other *N*-acyl derivatives of carbazole and diphenylamine are used for the chloranil condensation, the sulfonated dyes dye wool, silk, cotton, viscose, and paper in violet-blue shades.[58] Amino derivatives of trinuclear cyclic compounds but not containing nitrogen as part of the ring system, e.g. 2-aminodiphenylene oxide, may be condensed with *p*-benzoquinone or its derivatives to give violet pigments, which on sulfonation yield dyes for wool, cotton, and viscose with good fastness to light. The calcium and barium salts of the sulfonic acids are pigments.[59] Aminoanilino-benzotriazoles or -pyrazoles have been used for the chloranil condensation to produce dyes which have affinity for both wool and cotton.[60]

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[53] Fierz-David, Brassel, and Probst, *Helv. Chim. Acta* **22**, 1348 (1939).

[54] SP 169,958–60.

[55] IG, BP 457,555.

[56] IG, BP 427,977.

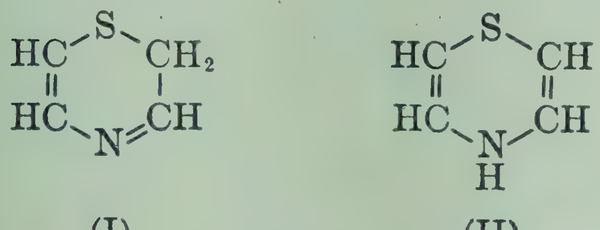
[57] IG, BP 452,033.

[58] IG, BP 415,749; SP 167,401–4; 170,343–6.

Fast brown leather dyestuffs with good penetrating power are obtained by condensing two moles of a nitroaminodiphenylaminedisulfonic acid with a *p*-benzoquinone derivative in the presence of an oxidizing agent;[61] these dyes may belong to the dioxazine class, but their constitution has not been investigated.

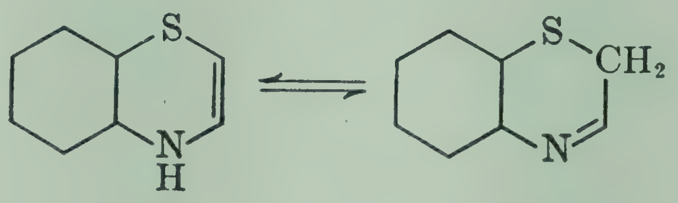
THIAZINES

1,4-Thiazine (b.p. 76.5–77°), which can exist in two forms (I) and (II), was synthesized for the first time very recently by the reduction of thiodiglycolimide.[62] 1,4-Benzothiazine (b.p. 236–238°) is prepared by condensing *o*-aminothiophenol with *α*,*β*-dibromoethylene in presence of alcoholic alkali.[63] Thiodiphenylamine (phenothiazine), the parent substance of the thiazine series, is made by baking diphenylamine with sulfur at about 180° (with excess of aluminum chloride if desired),[64] and is manufactured in large quantities for use as a veterinary anthelminthic.



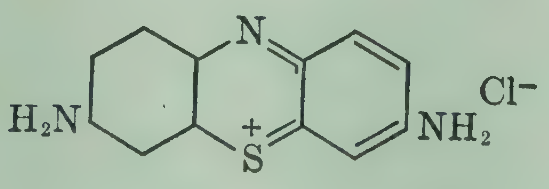
(I) (II)

1,4-Thiazine



1,4-Benzothiazine

Lauth's Violet (CI 920), the first dyestuff of the thiazine class, was prepared by Lauth (1876) by oxidation of *p*-phenylenediamine and hydrogen sulfide with ferric chloride in acid solution. This is a general reaction which may be used for the detection of *p*-diamines, as well as hydrogen sulfide, but it is not a practicable process. Lauth's Violet



Lauth's violet

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[59] IG, BP 437,283.

[60] du Pont, USP 2,336,520–1; 2,336,664.

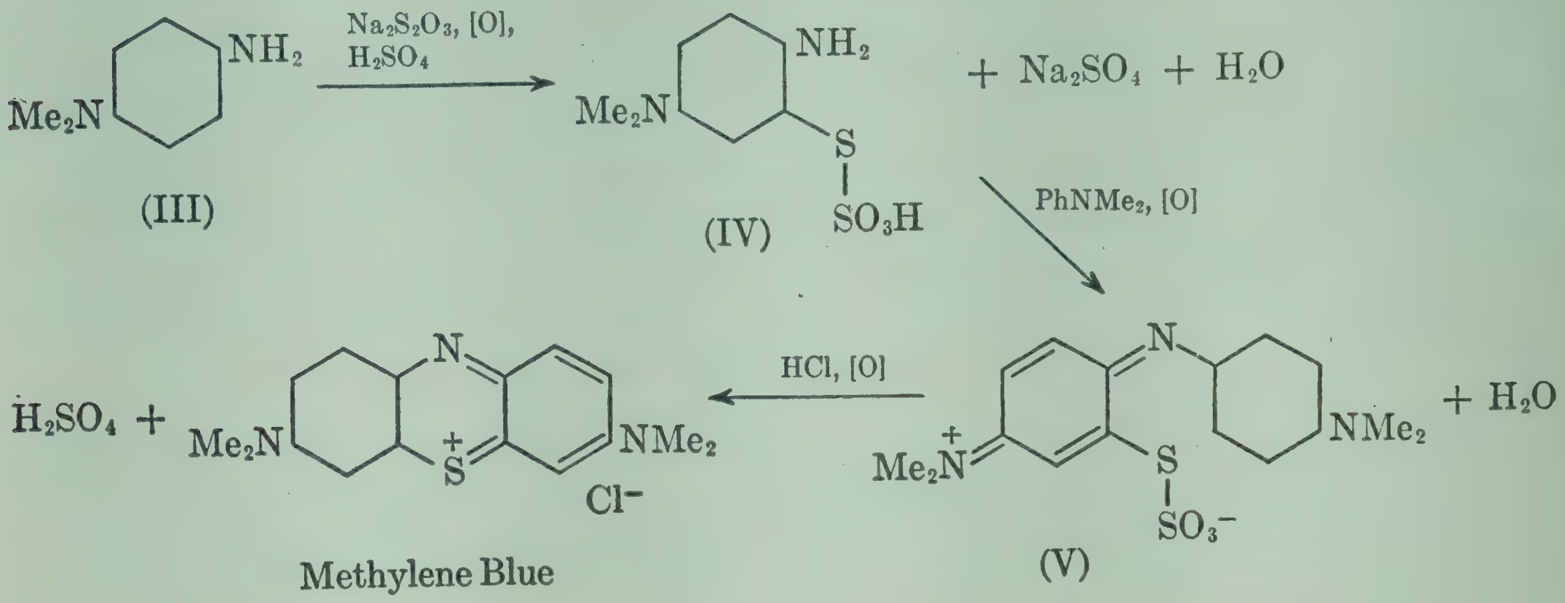
[61] IG, BP 453,509.

[62] Barkenbus and Landis, *JACS* **70,** 684 (1948).

[63] Unger, *Ber.* **30,** 609 (1897); Beilstein, 4th ed. **27,** p. 44.

[64] Vlugter and Overhof, DP 61,157.

itself is obsolete as a dye. Methylene Blue, discovered soon after (Caro, 1876; CI 922), is an important dye, first prepared from *p*-aminodimethylaniline (III) in the same way as Lauth's Violet. This was later replaced by Bernthsen's thiosulfate method, in which a mixture of dimethylaniline, (III) and sodium thiosulfate was oxidized with sodium dichromate and hydrochloric acid in the presence of zinc chloride. Better yields were obtained by the addition of aluminum sulfate, since aluminum thiosulfate dissociated readily and was a more effective agent than sodium thiosulfate for the thiosulfonation of (III) to (IV). The usual procedure is to treat dimethylaniline with sulfuric acid and sodium nitrite; reduce the nitroso compound to (III) by the addition of water and iron; filter off iron oxide sludge; convert (III) into the thio acid (IV) by treatment with sulfuric acid, dichromate and sodium thiosulfate at −1–3°; oxidize to the indamine (V) by adding dimethylaniline, sulfuric acid, dichromate and copper sulfate and heating to about 90°; finally convert the indamine into Methylene Blue by the addition of hydrochloric acid and zinc chloride to the blue solution at 45°, and salt out the dye.[4]



Both the Lauth and Bernthsen processes involve thionation and oxidation; the usual thionation process with sodium sulfide and sulfur employed in the preparation of the sulfide dyes also leads to the formation of thiazine rings when the intermediate is an indamine or indophenol, but the Methylene Blue type of thiazine dye is grouped separately from the sulfide dyes, and in the same class as azine and oxazine dyes to which they are allied in their constitution and dyeing properties. The Bernthsen synthesis is a general reaction applicable to other mixtures of monamines and *p*-diamines, leading to a series of blue basic dyes. Sulfonation of the residue obtained in the preparation of Methylene Blue is stated to yield a useful acid dye.[65]

Methylene Blue is marketed as the zinc chloride double salt for dyeing, and as the zinc-free hydrochloride for calico printing. A hydrochloride of 99.7% purity can be obtained by treatment of the commercial zinc chloride double salt with sodium carbonate, crystallizing from dilute hydrochloric acid, and recrystallizing from alcohol. Because of the brightness and purity of the shades, Methylene Blue is extensively used for dyeing and printing cotton on tannin or the Katanol type of mordant, and to a minor extent for dyeing silk, in spite of the low light fastness characteristic of the basic dyes as a class. Methylene Blue lakes are valuable in the nontextile coloring industries. The dye has no affinity for unmordanted cotton; but oxycellulose and cellulose containing mineral matter or combined acid are stained by the dye, and Methylene Blue absorption under standard conditions is useful for detecting and estimating modification in cellulose. The choice of Methylene Blue among the numerous basic dyes which exhibit similar behavior is based on the ease with which Methylene Blue may be prepared in analytically pure form. It is an oxidation-reduction indicator, and may be employed for instance in titanous chloride titrations, and in iodimetry in place of starch. Methylene Blue can be estimated directly by means of titanous chloride. Another method is to take advantage of its forming an insoluble dichromate, which may be weighed; or volumetrically, by treatment with excess of potassium dichromate and determining the excess by means of potassium iodide-thiosulfate.[66] The insoluble perchlorate can also be utilized for gravimetric assay of Methylene Blue.[67]

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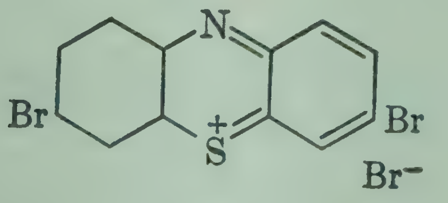
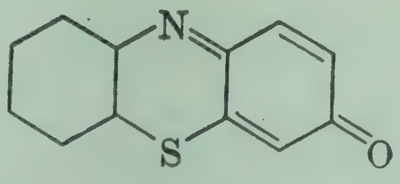
[65] Podkietnov, RP 66,442.

Methylene Blue is useful as a vital stain, since it deeply colors certain parts of the living tissue, such as the peripheral nervous system, leaving other parts unstained. It is one of the common stains in bacteriological technique for the examination of pathogenic organisms such as tubercular and cholera bacilli. Methylene Blue is a reagent for testing tubercular infection in milk; tuberculin-tested milk must not decolorize a standard aqueous solution of the dye within a stated period. The dye was used at one time as an analgesic and a urinary antiseptic, and it still seems to find some use as an antimalarial agent, especially in tertian and quartan malaria. As a weak and slow-acting antiseptic, it is also useful for external application in skin diseases.

The genetical relationship of thiodiphenylamine to Methylene Blue is shown by an old synthesis due to Kehrmann; by the action of excess of bromine, the former is converted into 3,7-dibromophenothiazinium


(VI)


Thionol

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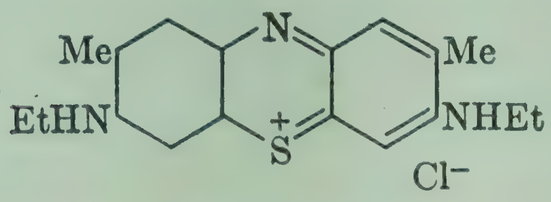
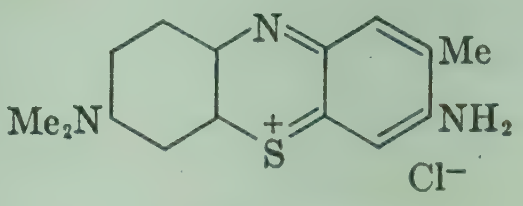
[66] Ferrey, *Quart. J. Pharm.* **16,** 208 (1943).

[67] Maurina and Deahl, *J. Am. Pharm. Assoc.* **32,** 301 (1943).

bromide (VI), which on heating with dimethylamine gives Methylene Blue as the bromide. Thionol, made by oxidizing thiodiphenylamine with hydrogen peroxide or ferric chloride in aqueous alcoholic hydrochloric acid, is a useful redox indicator.[68]

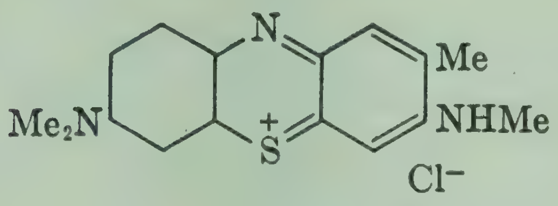


New Methylene Blue

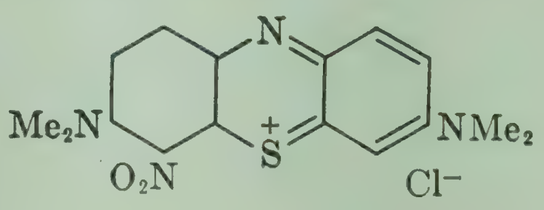


Toluidine Blue

The Methylene Blue analog using *N*-monoethyl-*o*-toluidine and its *p*-amino derivative is New Methylene Blue (Methylene Blue NN) (Weinberg, 1891) (B; CI 927), which gives a redder shade with better fastness to light than Methylene Blue. When *p*-aminodimethylanilinethiosulfonic acid is condensed with *o*-toluidine, the product is Toluidine Blue 0 (MLB; IG; CI 925). Methylene Blue MT (IG), formed by condensing *p*-aminodimethylanilinethiosulfonic acid with methyl-*o*-toluidine,[9] possesses exceptionally high solubility in cold water and is very suitable for producing hectograph inks. Its tinctorial power is stated to be about 25% greater than that of the isomeric Methylene Blue.[69] If *p*-aminodimethylaniline is condensed with diethylaniline, the product is Methylene Blue 2AM (Thionine Blue GO) (IG); according to CI 926, Thionine Blue GO (MLB)was the analog from methylethylaniline.



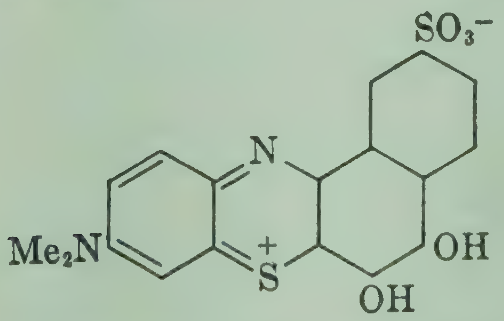
Methylene Blue MT



Methylene Green

When Methylene Blue is treated with nitrous and nitric acid, Methylene Green, which is perhaps the fastest green basic dye, is obtained.

Acid colors of the thiazine series are obtained by using amines containing a sulfonic group in the Bernthsen synthesis. Thus a mixture of *p*-sulfobenzylethylaniline and its *p*-amino derivative gives·the blue acid dye, Thiocarmine R (CI 928), which is no longer used. Brilliant Aliza-



Brilliant Alizarin Blue 3R

[68] Granick and Michaelis, *JACS* **69**, 2983 (1947).

[69] IG, BP 446,574.

rine Blue 3R (Heymann, 1892) (By; CI 931) is an acid-mordant color obtained by condensing *p*-aminodimethylaniline thiosulfonic acid with 1,2-naphthoquinone-6-sulfonic acid. Indochromogen S is the diethyl homolog. These dye reddish blue to greenish blue shades on chrome-mordanted wool, and are also useful in calico printing; the bright blue chrome lakes are dischargeable by chlorate and yellow prussiate.

Chapter XXVI

BENZOPHENONE, BENZOQUINONE AND NAPHTHOQUINONE DYES

Alizarin Yellow C (Nencki and Sieber, 1881) (B; CI 1013), one of the earliest synthetic mordant dyes, was gallacetophenone, obtained by heating pyrogallol with acetic acid and zinc chloride (the Nencki reaction).[1] It gave a yellow on aluminum mordant with moderate fastness to all agencies except light. A similar dye was Alizarin Yellow A (BASF; CI 1014), gallobenzophenone, prepared by the action of benzotrichloride and zinc chloride on pyrogallol. Both these dyes had some use in calico printing, but have now been displaced by the azo mordant yellows.

The hydroxy derivatives of benzoquinone possess mordant dyeing properties, but are not of commercial value. When *p*-benzoquinone is treated with *p*-chloroaniline in water in presence of manganese acetate, the usual indirect quinonoid addition takes place and the product is the hydroquinone derivative (I). Oxidation with hydrogen peroxide gives the corresponding quinone which is mixed with hydrosulfite and marketed as a vat dye, Helindone Yellow CG or CM vat powder (MLB) (Lesser, 1910).[2] Sulfurization of (I) gives brown and khaki dyes.[3]

In the naphthalene series, Naphthazarin (Brilliant Alizarin Black B) (Roussin, 1861) (BASF; CI 1019), a dye of considerable importance at one time, can be prepared by heating a mixture of 1,5- and 1,8-dinitronaphthalene with fuming sulfuric acid and flowers of sulfur. It is obtained in 59% yield by dissolving 1,5-dinitronaphthalene (20 g.) in monohydrate (400 g.) and adding below 40° a solution of sulfur (7 g.) in 66% oleum (120 g.); on pouring into ice after 30 minutes, filtering, and boiling the filtrate, Naphthazarin separates and is purified by drying and subliming at 170–180° under reduced pressure.[4] Naphthazarin sublimes in brown needles with a green luster, which dissolve in aqueous caustic soda with a cornflower-blue color and in sulfuric acid with a magenta color. For a long time Naphthazarin was regarded as 5,6-dihydroxy-

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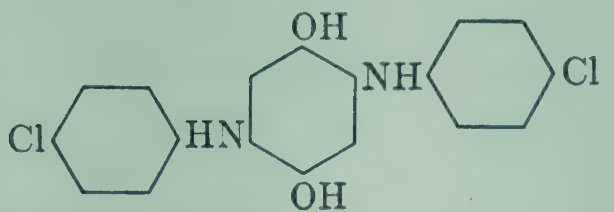
[1] Badhwar and Venkataraman, *OSCV* II, p. 304.

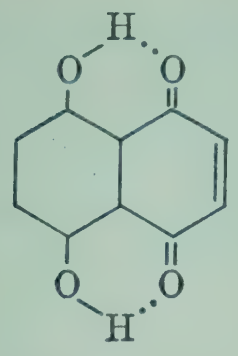
[2] *BIOS* **1493**.

[3] See Chapter XXXVI.

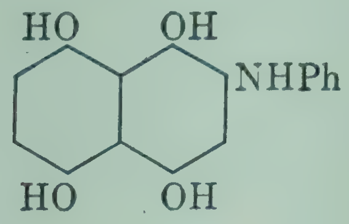
[4] Fierz-David and Stockar, *Helv. Chim. Acta* **26**, 92 (1943); see also Bayer, DRP 71,386.



(I)



Naphthazarin



Alizarin Black SRA

1,4-naphthoquinone, but Dimroth and Ruck in 1925 showed that it is the 5,8-dihydroxy compound, since it contains two chelate groups, forming for instance a di-ester with boric acid, while the 5,6-isomer would only give a mono-ester; further, it is not an *o*-dihydroxy compound since it does not form an azine with *o*-phenylenediamine.[5] This has been confirmed by the synthesis of Naphthazarin by condensing hydroquinone with maleic anhydride in presence of aluminum chloride and sodium chloride.[6] From a study of the absorption spectra[7] and the crystal structure,[8] it has been shown that Naphthazarin has the indicated hydrogen bonded structure. Naphthazarin is insoluble in water, and was utilized as a dye only when the soluble bisulfite compound, Alizarin Black S (BASF, 1887), was prepared. It is used for dyeing wool on a chrome mordant, the black thus obtained being fast to washing and milling and particularly fast to acid. Reduction of Naphthazarin gives Alizarin Black WX (Bohn, 1900) (BASF; CI 1020), 1,4,5,8-tetrahydroxynaphthalene, which dyes wool and silk from an acetic acid bath, afterchromed to a level black, which has good all-round fastness. The bisulfite compound of this dye, Brilliant Alizarin Black (BASF; CI 1019), is water-soluble and it can be used with chromium acetate for gray to blue-black shades in calico printing. Naphthazarin, being a quinone, combines readily with amines and phenols, and other dyes are thus obtained. Alizarin Black SRA (Bohn, 1897) (BASF; CI 1022) which is the 2-anilino derivative of Alizarin Black WX, and is obtained by heating Naphthazarin with aniline hydrochloride in presence of boric acid, dyes wool black on a chrome mordant, and the black is faster to chlorine than the Naphthazarin black. The similar compound from phenol is Alizarin Dark Green W (Bally, 1897) (BASF; CI 1023), which dyes chrome-mordanted wool gray-green to greenish black of good fastness. While these naphthoquinone derivatives are of little technical importance at

[5] Dimroth and Ruck, *Ann.* **446,** 123 (1925).

[6] Zahn and Ochwat, *Ann.* **462,** 72 (1928).

[7] Morton and Earlam, *JCS* 159 (**1941**).

[8] Palacios and Salvia, *Anales soc. esp. fis y quim.* **32,** 49 (1934).

the present time, many of the azo chrome dyes, by which they have been replaced, are converted into derivatives of 5-hydroxy- or 5,8-dihydroxy-1,4-naphthoquinone by oxidation of the dyes on the fiber. The monosodium salt of chromotropic acid was marketed by MLB as Chromogen I (Kuzel, 1890) (MLB; CI 1026); applied to wool and afterchromed, brown shades were produced owing to the formation of a chromium complex of 8-hydroxy-1,4-naphthoquinone-3,6-disulfonic acid.

The Naphthazarin melt has to be boiled with water to give Naphthazarin, and the intermediate product can be isolated,[9] and used for making other dyestuffs. Thus the acid color, Acid Alizarin Grey G (IG), is made by heating 1,5-dinitronaphthalene with sulfuric acid and sulfur at 105–108° for 12 hours, filtering off the sulfur, pouring the filtrate into ice, and salting out the product as the zinc chloride double salt. This is treated with aniline and aniline salt at room temperature for 3 hours, then heated for 6 hours at 90–115°, and finally sulfonated.[10] Brominated naphthoquinonimines can be prepared by treating the dinitronaphthalenes with sulfur, oleum, bromine and a trace of iodine.[10a] By condensing 3,6-dibromo-5-amino-8-hydroxy-1,4-naphthoquinone-1-imine with arylamines, phenols or thiophenols, products useful as dyes or dye intermediates are obtained.[10b]

Naphthazarin derivatives have recently been suggested as cellulose acetate dyes. Celliton Fast Green 3B, one of the IG range of cellulose acetate dyes, is the condensation product of *p*-aminophenyl benzyl ether and 5-amino-8-hydroxy-1,4-naphthoquinonediimine. The latter is prepared by heating 1,5-dinitronaphthalene with oleum and sulfur at 15–45°, filtering off sulfur, and precipitating the base by neutralization.[10c] The reactive 5,8-dihydroxy-1,4-naphthoquinone or its substituted derivatives may be condensed with amines of the type $NH_2{-}(CH_2)_n{-}X$, where X = furyl or tetrahydrofuryl attached to CH_2 at position 2; this introduces the amine at the 2-position in Naphthazarin and also at 5 or 8 or both, the resulting products being dyes for cellulose acetate, of shades varying from bluish-red to bluish-green.[11] The phosphoric esters of 5-hydroxy-1,4-naphthoquinones carrying hydroxyalkylamino groups at positions 2 and 8 are cellulose acetate dyes.[11a]

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[9] BASF, DRP 101,372; 108,551–2; MLB, DRP 111,683.

[10] *BIOS* **987.**

[10a] Sandoz, BP 606,008; 629,706.

[10b] Sandoz and May, BP 613,076; 633,663.

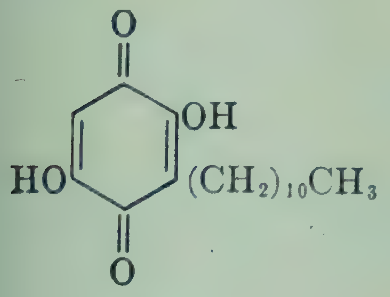
[10c] *BIOS* **1484.**

[11] Dickey, McNally, and Eastman Kodak, USP 2,275,741.

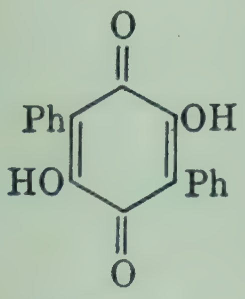
[11a] Eastman Kodak, USP 2,301,382.

NATURALLY OCCURRING DERIVATIVES[12, 13]

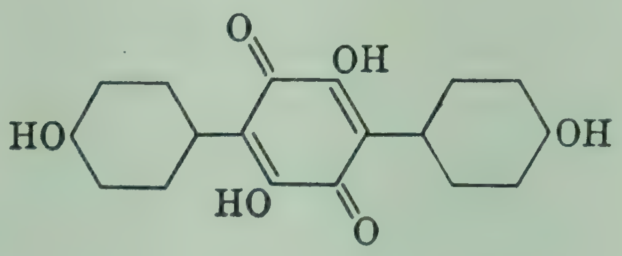
Many benzoquinone and naphthoquinone derivatives occur in nature, and several of them exhibit interesting antibiotic and physiological properties, which may possibly be connected with their reversible reduction-oxidation systems. 2,6-Dimethoxybenzoquinone has been isolated from *Herba adonis vernalis* and synthesized by the oxidation of pyrogallol trimethyl ether with nitric acid and ethanol.[12] Embelin, the bright yellow active principle of the berries of *Embelia ribes*, is used as a remedy for tape worms; it has been synthesized by the interaction of 2,5-dihydroxybenzoquinone and dilauroyl peroxide.[14] The alkylation of quinones with a diacyl peroxide (e.g., *C*-methylation with acetyl peroxide) or a lead tetraacylate (replaceable by a fatty acid, red lead and a promoter such as malonic acid or methanol) is a valuable general reaction which has been applied with great success to synthesis in the naphthoquinone series (Fieser, 1942). The tridecyl homolog[14, 15] of embelin occurs as the pigment rapanone in the bark of *Rapanea maximowiczii*. The orange-red coloring matter, maesaquinone, in the fruits of *Maesa japonica* is apparently the C_{20} homolog. Perezone, isolated from the roots of Mexican species of *Perezonia*, is a 2-hydroxy-3-methyl-1,4-benzoquinone with an alkenyl chain ($-CHMe-CH_2CH_2CH=CMe_2$) in the 6-position.[12] Kögl has isolated several benzoquinones derived from terphenyl from mushrooms, e.g., polyporic acid, atromentin and muscarufin. Fungi of the *Thelephora* species contain the reddish black thelephoric acid, the constitution of which has been shown by Kögl to be a 1,4,7-trihydroxyphenanthraquinone-6-carboxylic acid with a diene acid chain ($-CH=CH-CH=CH-COOH$) in the 2-position.[12]



Embelin



Polyporic acid



Atromentin

Among the metabolic products of moulds many benzoquinone derivatives have been encountered. The maroon colored fumigatin (from *Aspergillus fumigatus*), the nearly black spinulosin (from *Penicillium spinulosum*) and the red phoenicin (from *Penicillium phoeniceum*) are examples.[12]

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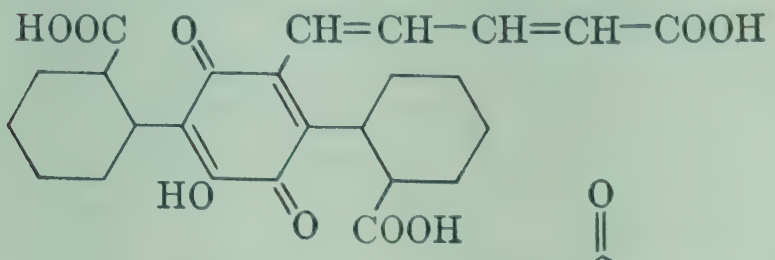
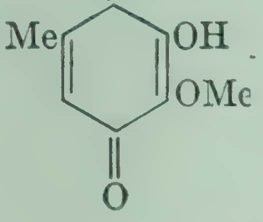
[12] For Refs. see Ref. 1, Chapter XXIV.

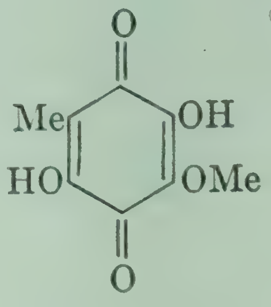
[13] For a detailed account of benzoquinones and naphthoquinones, including the naturally occurring derivatives, see Fieser and Fieser, Organic Chemistry, Heath, Boston, 1950.

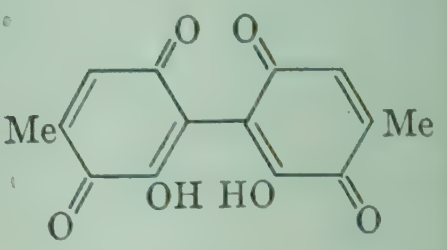
[14] Fieser and Chamberlain, *JACS* **70,** 71 (1948).

[15] Asano and Yamaguti, *J. Pharm. Soc. Japan* **60,** 585 (1940).

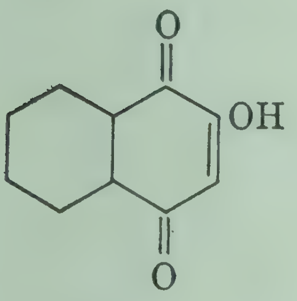

Muscarufin

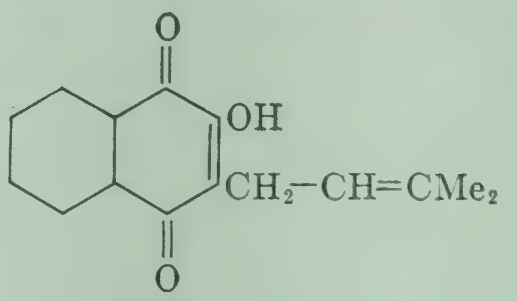

Fumigatin

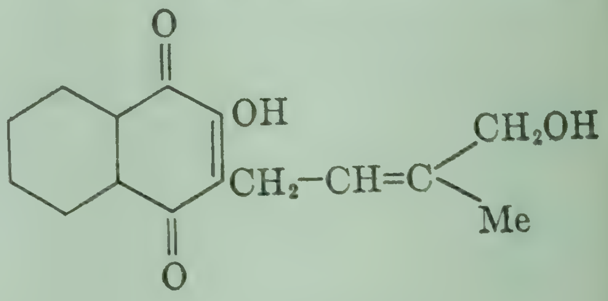

Spinulosin


Phoenicin

The simplest naphthoquinones isolated from nature are lawsone, the coloring matter of henna, and juglone found as the dihydro compound (1,4,5-trihydroxynaphthalene) in the green parts of the walnut tree (*Juglans regia*).[12] Juglone (5-hydroxy-1,4-naphthoquinone) is a powerful fungicide,[16] and its use in the treatment of skin diseases has been mentioned.[17] Henna has the properties of an acid dye and finds considerable use for dyeing hair. Hennas compounded with indigo, pyrogallol or copper salts are sold for the purpose.[18] Plumbagin (from the root of *Plumbago rosea*) is 2-methyljuglone,[12] and it has antibacterial and medicinal properties.[19] Lapachol (from the Lapacho and other trees) has been synthesized by the interaction of the silver salt of 2-hydroxy-1,4-naphthoquinone (lawsone) and isoprene hydrobromide.[12] Lomatiol, the coloring matter of the seeds of *Lomatia illicifolia*, is closely allied to lapachol, being an ω-hydroxylapachol. A conversion of lapachol to lomatiol has been recently accomplished.[20] A remarkable general reaction of lapachol and other alkyl and β-alkenyl derivatives of hydroxy-


Lawsone


Lapachol


Lomatiol

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[16] Gries, *Northern Nut Growers Assoc. Ann. Rept.* **34,** 52 (1943).

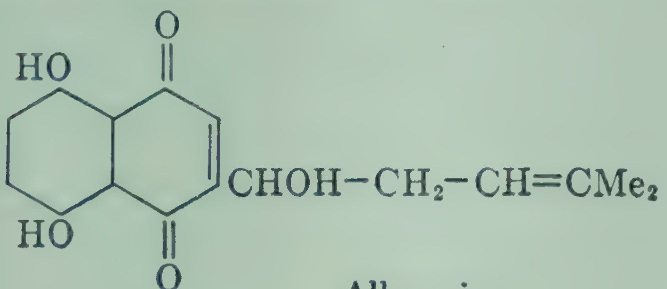
[17] Brissemoret and Michaud, *J. pharm. chim.* **16,** 283 (1917).

[18] Cox, *Analyst* **63,** 397 (1938).

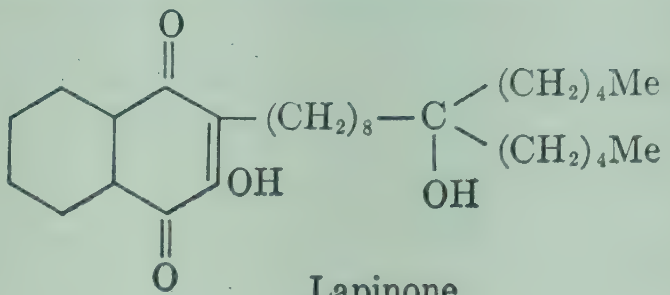
[19] Saint-Rat, Olivier, and Chouteau, *Bull. acad. méd.* **130,** 57 (1946).

[20] Gates, *JACS* **70,** 617 (1948).

naphthoquinone is the Hooker permanganate oxidation which results in the elimination of a methylene group; thus lapachol gives 3-(β,β-dimethylvinyl)-2-hydroxy-1,4-naphthoquinone, the double bond being left intact.[21] An ancient dyestuff, which defied purification and was assigned widely different molecular formulas over many years, is the dark red alkannin (anchusin), the essential constituent of alkanet, the root of *Alkanna* or *Anchusa tinctoria.* Alkannin has now been shown to be a relatively simple Naphthazarin derivative, and structurally identical with shikonin (Tokyo Violet), the coloring matter of the Japanese plant *Lithospermium erythrorhizone;* alkannin and shikonin are optical enantiomorphs (Brockmann, 1935).[12] Droserone, one of the two coloring matters occurring in *Drosera Whittakeri*, is 3,5-dihydroxy-2-methyl-1,4-naphthoquinone, and it has been synthesized by the acetyl peroxide alkylation of 3-hydroxyjuglone, which is prepared by hydrolysis of 3-chlorojuglone.[22] The second pigment is the 8-hydroxy derivative of droserone, synthesized by condensing maleic anhydride and 2-methoxy-3-methylhydroquinone in a sodium-aluminum chloride melt.[12]

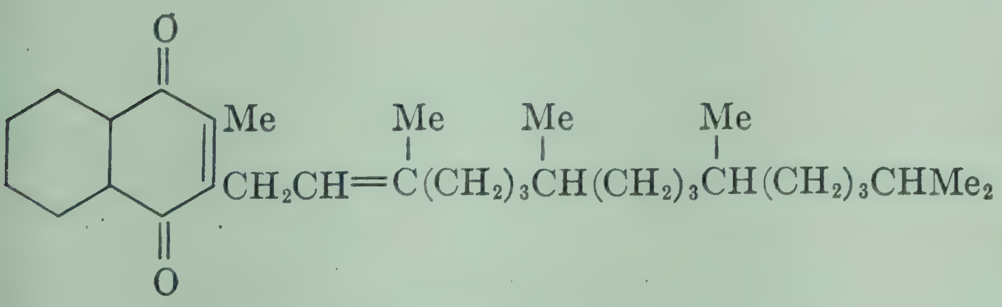


Alkannin

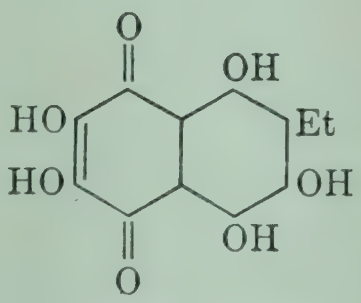


Lapinone

Vitamin K_1 and K_2 are derivatives of 1,4-naphthoquinone, and the naphthoquinone coloring matters such as lapachol and lomatiol exhibit vitamin K activity. Fieser has explained the characteristic transient blue coloration of vitamin K_1 and K_2 and other β-alkenylnaphthoquinones with sodium ethylate as being due to the replacement of the unsaturated side chain by a hydroxyl group, resulting in the formation of pigments similar to phthiocol (2-hydroxy-3-methyl-1,4-naphthoquinone), which has been isolated from human tubercle bacilli. The pigment Echino-



Vitamin K_1



Echinochrome A

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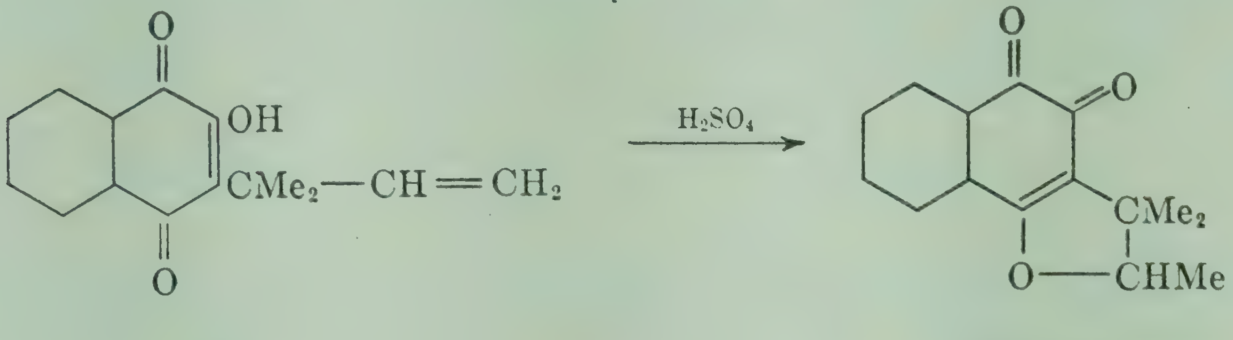
[21] For a study of the mechanism of the Hooker oxidation, see Fieser and Fieser, *JACS* **70,** 3215 (1948).

[22] Thomson, *JCS* 1277 (**1949**).

chrome A occurs in sea urchin eggs, and one of the two possible *p*-quinone forms is indicated.[23]

Starting from the clue that dihydrolapachol possesses mild antimalarial activity, Fieser and his collaborators have investigated nearly three hundred 2-hydroxy-3-alkyl-1,4-naphthoquinones; the most potent compound (lapinone) was a hundred times as active as dihydrolapachol.[24]

Dunnione, the orange-red pigment occurring as a deposit on the leaves of *Streptocarpus Dunnii,* is a β-naphthoquinone derivative.[12] Racemic dunnione has been synthesized by cyclization of (I) obtained



(I) Dunnione

by a Claisen rearrangement of the appropriate ether of 2-hydroxy-1,4-naphthoquinone.[25]

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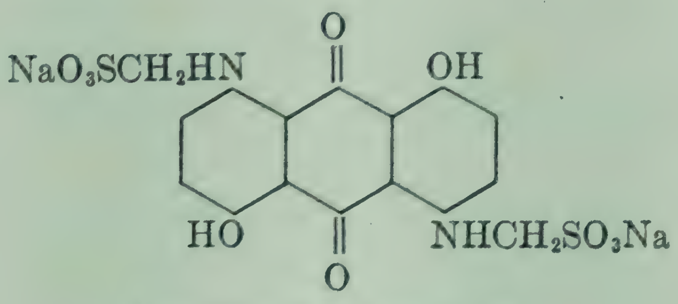
[23] Kuhn and Wallenfels, *Ber.* **72,** 1407 (1939).
[24] Fieser *et al., JACS* **70,** 3151 (1948); *et seq.*
[25] Cooke, *Nature* **162,** 178 (1948).

CHAPTER XXVII

ANTHRAQUINONE DYES FOR CELLULOSE ACETATE

The characteristic properties of dyes suitable for application to cellulose acetate rayon have been discussed earlier.[1] Like the insoluble azo dyes, aminoanthraquinones and aminohydroxyanthraquinones were first utilized by converting them into the Ionamine type by a formaldehyde-bisulfite condensation. Ionamine Pure Blue R and G were prepared by the treatment of 4,8-diamino-1,5-dihydroxyanthraquinone and 4,5-diamino-1,8-dihydroxyanthraquinone respectively with formaldehyde and sodium bisulfite. Although the Ionamines are obsolete, the solubilization of aminoanthraquinones as the methanesulfonates and their isolation in purer form by working in organic solvents, or by interaction with formaldehyde in phenol solution and then sulfonating, have been mentioned in recent patents.[2] When the dispersed azo dyes for cellulose acetate (Dispersol and S.R.A. dyes)[1] were developed in 1923, it was found that the dispersion process was applicable to simple anthraquinone derivatives as well as to azo dyes; the anthraquinones were absorbed by cellulose acetate rayon equally readily and the shades were much faster. Thus a 10% paste of α-aminoanthraquinone in water containing 2–3% of a dispersing agent was an early example of a cellulose acetate dye, giving yellow shades from a soap bath at about 80°. The Duranol colors (BDC, ICI), Celatene dyes (SD) and some of the S.R.A. colors (British Celanese Co.) are such dispersions of amino- and aminohydroxyanthraquinones, and anthraquinone derivatives have since been



Ionamine Pure Blue R

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[1] See Chapter XXI.

[2] Sandoz, BP 529,355; 536,303.

included in the cellulose acetate range of other dye manufacturers. Many of these dyes are applicable to nylon. The problem of preparing stable dispersions of insoluble or sparingly soluble dyes has been approached from two sides.[1] One is the use of more powerful dispersing agents (e.g., condensation products of alkylnaphthalenesulfonic acids and formaldehyde) and the improvement of methods of dispersion; a simple and effective method of dispersion, e.g. of 1,4,5,8-tetraminoanthraquinone, is to dissolve the dye in tetrahydrofuran and add to soap solution.[3] The other is the attachment of alkanol, carboxyl, amide and other groups to the dye molecules in order to render the dyes more readily dispersible. The introduction of hydroxyalkyl and other groups sometimes also effects increased affinity, improved leveling, and minor modifications in shade. Cellulose acetate dyes may be marketed as paste or powder brands, and the latter may be produced by drying down the aqueous dispersions. For dyeing, the dyestuff is pasted up with soap, Turkey Red oil or a wetting agent, and the dyebath is made up with water containing one of these dispersing agents.[1]

AMINOANTHRAQUINONE DERIVATIVES

The range of shades obtainable from the simple amino- and aminohydroxyanthraquinones is indicated in Table I. Anthraquinone dyes for cellulose acetate derived from 1,4-diaminoanthraquinone are violet, blue and green dyes with good affinity, level-dyeing power and excellent fastness. Further, the usual type is unsymmetrically substituted by alkyl or aryl groups on the two nitrogen atoms. The main method of preparation is the condensation of quinizarin, 1-amino-4-hydroxyanthraquinone, 1,4-diaminoanthraquinone or their leuco derivatives with primary amines.[4] In dyeing acetate rayon blue shades using 1,4-dialkylaminoanthraquinones, a mixture of two or three dyes gives brighter and more intense shades than any of the components.[5] 1,5-Diamino-4,8-dihydroxyanthraquinone (4,8-diaminoanthrarufin) is best prepared by the nitration and reduction of 1,5-diphenoxyanthraquinone. Nitration yields a hexanitro compound in which, besides two nitro groups in the 4,8-positions of the anthraquinone nucleus, two nitro groups enter each of the phenyl groups. Hydrolysis with dilute caustic soda solution then gives very pure 4,8-dinitroanthrarufin, which is finally reduced to the diamine by means of sodium sulfide.[6]

While anthraquinone derivatives are principally employed for violet,

[3] Societe Rhodiaceta, BP 596,264.

[4] IG, BP 447,037; 447,088; 447,107–8; 461,428.

[5] IG, BP 452,421.

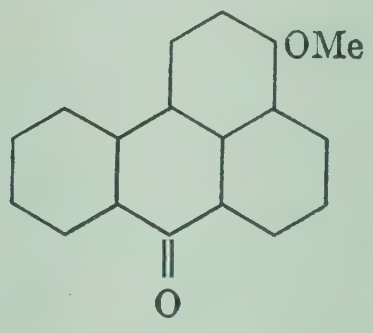
[6] DRP 158,531; 170,728.

TABLE I

AMINOANTHRAQUINONES AS CELLULOSE ACETATE DYES[7, 8]

Anthraquinone derivative	*Shade or commercial name*
1-Amino	Yellow
1-Amino-2-methyl	Orange
1-*N*-Methylamino	Celliton Orange R; Duranol Red G
1-Amino-2-hydroxy-4-methoxy	Yellowish rose
1,5-Diamino	Red
1-Amino-4-hydroxy-2-methoxy	Celliton Fast Pink RF
1,4-Diamino-2-methoxy	Celliton Fast Pink FF3B; Duranol Red X3B
1-Amino-4-hydroxy	Celliton Fast Pink B
1,4-Diamino	Celliton Fast Red Violet R
5-Nitro-1,4-diamino	Celliton Fast Violet B
1-Amino-4-*N*-methylamino	Purple
Partially methylated 1,4-diamino	Celliton Fast Violet 6B
1-Amino-4-acetamido	Violet
1,4-Bismethylamino	Celliton Fast Blue B; Duranol Blue B
1,5-Diamino-4,8-dihydroxy	Blue
4,5-Diamino-1,8-dihydroxy	Blue
1,4,5,8-Tetramino	Celliton Blue extra; Duranol Brilliant Blue CB
Methylated 1,4,5,8-tetramino	Celliton Blue 3G
1,5-Bismethylamino-4,8-dihydroxy	Duranol Blue G
1-Methylamino-4-*p*-aminoanilino	Green

blue and green shades, the less deep shades (yellow to red) being obtained from azo dyes, it will be noticed that the series include orange and red shades. An interesting example of a yellow dye for cellulose acetate derived from anthraquinone is 3-methoxybenzanthrone (Duranol Brilliant Yellow 3G, ICI), which however is not in the current commercial range. 3-Methoxybenzanthrone yields fast greenish yellow shades



Duranol Brilliant Yellow 3G

1,
sing

and may also be used in mixtures with blue anthraquinone acetat enol in dyes for green shades.[9] *N*-Acyl derivatives of 1-amino-5- and 8 anthraquinone are yellow dyes for cellulose acetate and n aliphatic (e.g., acetic, propionic) acid is used for acyl

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[7] *BIOS* **1484.**

[8] For an empirical correlation of the color and constitution of anthra tives, see Houben, Anthracene and Anthraquinone, Georg Thieme

[9] ICI, BP 447,134.

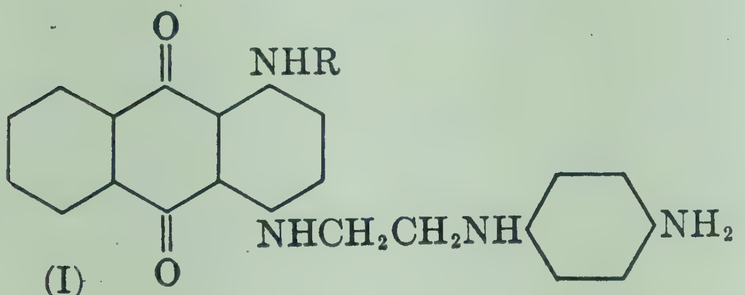
[9a] Ciba, BP 639,223; 639,250.

dihydropyrimidine derivatives obtained by condensing *o*-aminocyanoanthraquinones with aldehydes are substantive to acetate rayon, and many of them are yellow dyes.[10] Aminoanthrapyrimidines dye acetate silk in greenish yellow to red shades; and methods for the halogenation of aminoanthrapyrimidines,[11] the preparation of polyaminoanthrapyrimidines by aminating aminoanthrapyrimidinesulfonic acids,[12] and for converting anthrapyrimidines into hydroxy derivatives, which also dye acetate rayon in yellow shades, by treatment with sulfuric acid in presence of catalysts,[13] have been described. Red anthrapyridone dyes for cellulose acetate are obtained by condensing a 4-bromo-6-anilinoanthrapyridone, in which the anilino group may be substituted in the ring or on the nitrogen, with a phenol or naphthol; sulfonation gives wool dyes.[14] A red dye with good fastness to gas fumes is obtained by methylating 1-amino-4-hydroxy-2-mercaptoanthraquinone.[14a] The mixed ureas derived from 1,5-diamino-4,8-dihydroxyanthraquinone or 4,5-diamino-1,8-dihydroxyanthraquinone and α-aminoanthraquinone yield brown shades.[15]

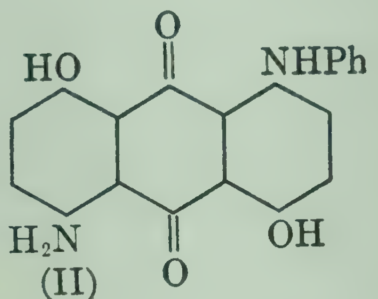
Aminoanthraquinones derived from 6-chloro- and 6,7-dichloroquinizarin have good fastness to light.[16] The alkyl, aryl and aralkyl substituents in the aminoanthraquinones used for dyeing cellulose acetate may be of varying complexity, as indicated in Table I. Violet to bluish red dyes containing an alkoxy group in the 2-position are obtained when a 1-aminoanthraquinone-2-sulfonic acid with an aminoalkylamino or arylamino group in the 4-position is treated with ethylene oxide, or a polymeride thereof, or with a mono- or polyhydric alcohol or carbohydrate, e.g. mannitol.[17] Alkylation of 1,4,5-tri- and 1,4,5,8-tetraminoanthraquinone leads to blue dyes.[18] The mixture of partially methylated amines obtained by the action of methanol and sulfuric acid on 1,4,5,8-tetraminoanthraquinone is a better dye for cellulose acetate than the parent amine.[18] 1,4,5,8-Tetrakismethylaminoanthraquinone, dark blue crystalline compound, has been prepared by heating 4,8-diamino-1,5-dimethoxyanthraquinone with methylamine in ethanol yie 180°.[19] 4,8-Diamino-1,5-bismethylaminoanthraquinone and 4,5-dia-
4,8-pc BP 483,585.
of the ph 449,537; 449,611.
gives very m. J. 52,786.
diamine by ,944.
odak, USP 2,268,814.
While a orp. of America, BP 639,266.

[3] Societe Rhoc lins, and British Dyestuffs, BP 248,858.
[4] IG, BP 447,(nd Sandoz, USP 2,433,551.
[5] IG, BP 452,4 ,013.
[6] DRP 158,531; 59.
6; see also Bayer, DRP 144,634; and Ref. 20.

mino-1,8-bismethylaminoanthraquinone have been synthesized recently.[20] It has been claimed[21] that anthraquinone derivatives containing one or two α-amino groups and an α-hydroxy group are specially resistant to light and fumes. Examples are 1-amino-4-anilino-5-hydroxy- and 1-amino-5-anilino-4,8-dihydroxyanthraquinones. The *o*-anisidino group gives better resistance than the anilino group,[22] and affinity is increased by acetylating an anilino group.[23] 4-Arylamino-1,5-dihydroxyanthraquinones, obtained by heating leuco-1,4,5-trihydroxyanthraquinone with an arylamine in an inert solvent (e.g., Cellosolve) at 80–120°, give blue shades on cellulose acetate, fast to gas fumes, and are also suitable for coloring alkylacrylate resins.[24] The introduction of a secondary alkylamino (e.g., isopropylamino) group instead of a primary alkylamino group in 1-amino-4-alkylaminoanthraquinone gives blue dyes with improved light fastness.[25] A further example is the blue dye (I), in which NHR may be the morpholino or tetrahydrofurfurylamino group.[26] The attachment of a phenyl or an *o*-methoxyphenyl residue to a nitrogen atom in aminoanthraquinones increases the fastness to light and to acid atmospheres, particularly sulfur dioxide fumes.[27] The blue dye (II) is prepared by heating 4,8-dinitroanthrarufin with aniline so as to replace one nitro group by the anilino group, and then reducing the second nitro group; and it is said to possess excellent fastness properties. The blue to blue-violet dyes obtained by condensing 4,8-dinitroanthrarufin (or other polynitrohydroxyanthraquinones) with sulfanilamide (or other aliphatic and aromatic amines) are fast to light and acid fading.[27a] 1-Amino-4-(*p*-hydroxyanilino)anthraquinone and its 1-alkyl, aryl, aralkyl, or cycloalkyl derivatives can be prepared by condensing 1-amino-4-hydroxyanthraquinone or a derivative with *p*-aminophenol in



(I)



(II)

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[20] Hall and Hey, *JCS* 736 (**1948**).

[21] Dreyfus, FP 750,838–9.

[22] Dreyfus, FP 750,840.

[23] Dreyfus, FP 750,841.

[24] Wuertz, Klein, and du Pont, USP 2,341,891.

[25] IG, BP 490,372.

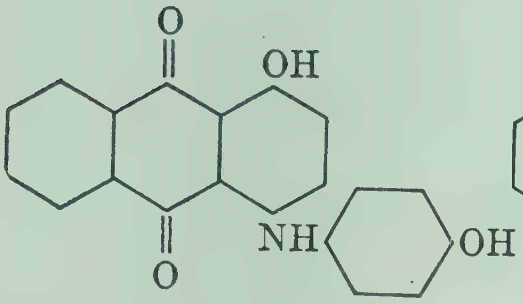
[26] Eastman Kodak, USP 2,311,065.

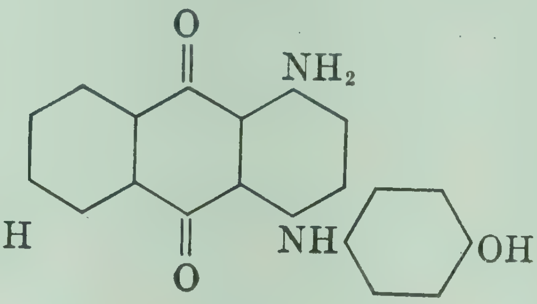
[27] British Celanese, BP 416,611–2; 420,591; 420,593.

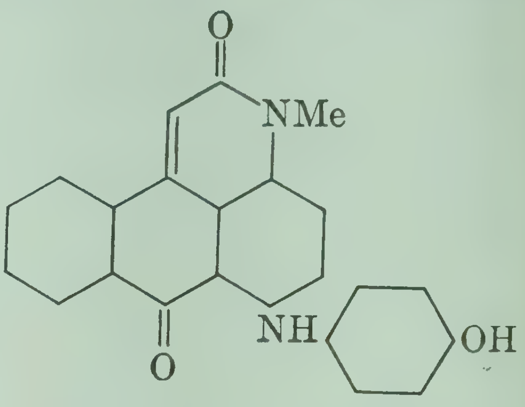
[27a] Seymour and Salvin, USP 2,480,269.

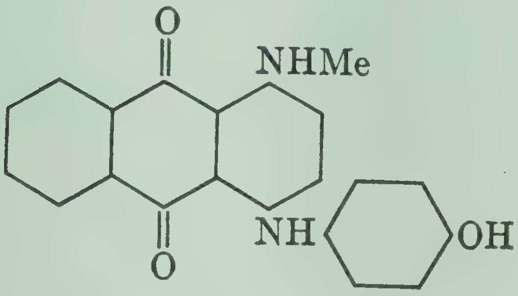
presence of boric acid and excess of a phenol as solvent; the products dye acetate rayon and, when sulfonated, are dyes for wool.[28]

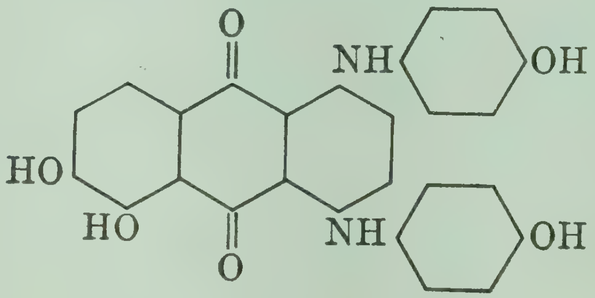
Among the Perlon Fast dyes developed by IG for use on Perlon, a nylon type synthetic fiber, a few are anthraquinone derivatives and these are also applicable to cellulose acetate. Examples are Perlon Fast Blue FFR and Blue FFB, Red Violet R, Green 3B and Green BT.[29]


Perlon Fast Blue FFR


Perlon Fast Blue FFB

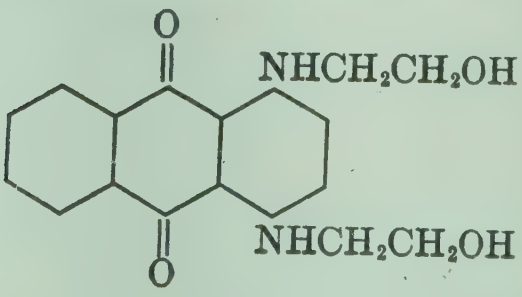

Perlon Fast Red Violet R

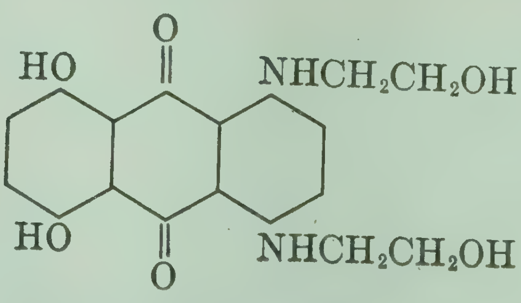

Perlon Fast Green 3B


Perlon Fast Green BT

Aminoanthraquinones Containing Hydrophilic Groups

A few examples of substituted aminoanthraquinones containing alkanol, carboxyl and other groups, which are introduced for the purpose of facilitating the dispersion of the dyes in water, may be quoted. As usual, the introduction of a large variety of groups has been suggested in the patent literature, but the principal substituent is the ethanolamine group. A method employed for the preparation of arylaminoanthraquinones,[30] which consists in heating quinizarin or leucoquinizarin with an amine, is suitable for the purpose. Thus the blue dye (III) is obtained

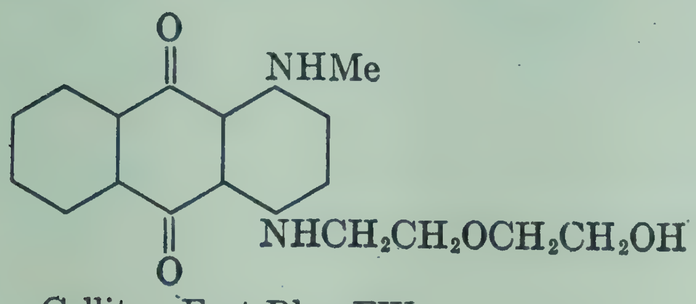

(III)


Celliton Fast Blue Green B

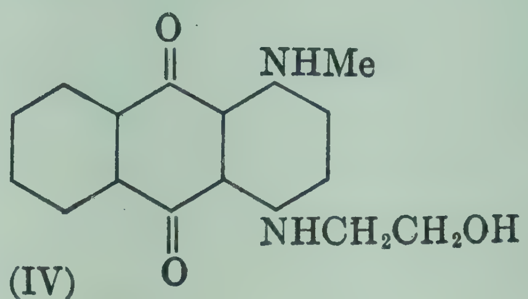
[3] Soci
[4] IG, .
[5] IG, B a, BP 536,885.
[6] DRP S Misc. Rept. 20.
Chapter XXIX.

by heating quinizarin with a 30% solution of monoethanolamine.[31] Celliton Fast Blue Green B is prepared similarly by heating leuco-1,4,5,8-tetrahydroxyanthraquinone with two moles of ethanolamine.[7]

The replacement of the hydroxyl groups in quinizarin may be carried out in two stages for the preparation of unsymmetrically substituted 1,4-diaminoanthraquinone derivatives. Celliton Fast Blue FW is an unsymmetrical derivative of 1,4-diaminoanthraquinone in which both the amino groups carry alkyl substituents. Celliton Fast Blue FFR is a mixture of (IV) which is the main constituent, 1,4-bismethylamino-anthraquinone and 1,4-bis-β-hydroxyethylaminoanthraquinone (III); such a mixture is appreciably stronger tinctorially than any of the components.[32] By heating leucoquinizarin with ethanolamine and methyl β-amino-*n*-butyrate in equimolecular amounts and oxidizing the product, we get a blue dye (V).[33] 1,4,5-Triamino-8-anthraquinonylglycine is an intense fast blue dye.[33a] 4-β-Hydroxyethylamino-1-diacetonylamino-anthraquinone is a blue dye.[34]

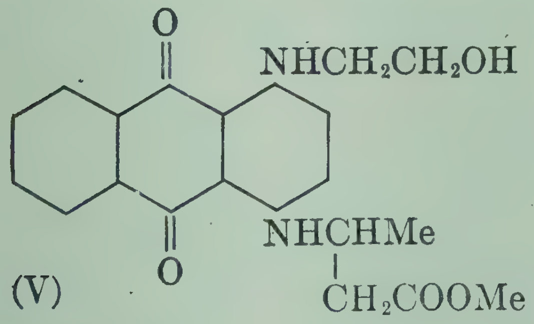


Celliton Fast Blue FW

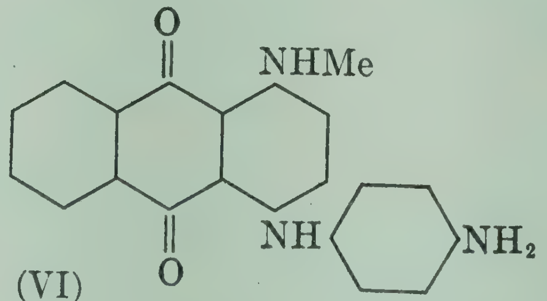


(IV)

Green or greenish blue shades are obtained from derivatives of 1,4-diaminoanthraquinone in which one amino group is substituted by hydroxyalkyl and the other by a hydroxy- or aminophenyl group. When the leuco derivative of quinizarin or 1,4,5-tri- or 1,4,5,8-tetra-hydroxyanthraquinone or a nuclear substituted derivative is treated with an alkylamine and an arylamine simultaneously or successively, the products are 4-arylamino-1-alkylaminoanthraquinones.[35] A green dye



(V)



(VI)

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[31] IG, BP 289,807.

[32] *BIOS* **987**, p. 155.

[33] Eastman Kodak, USP 2,319,043; for other variations see USP 2,191,029–30.

[33a] Ciba, SP 216,166.

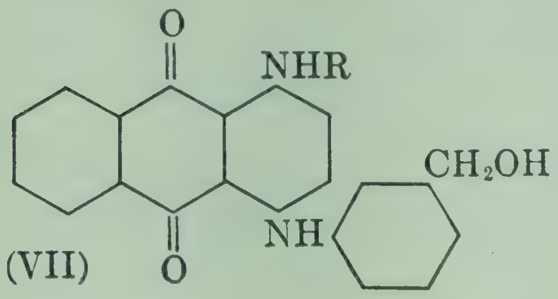
[34] Eastman Kodak, USP 2,384,889.

[35] Ciba, BP 425,450; 430,214; 429,951; 423,256.

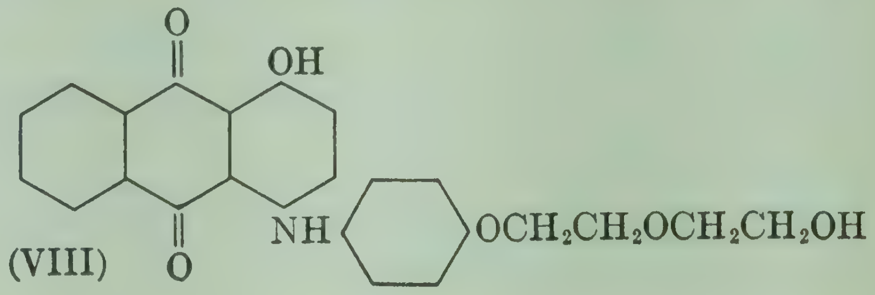
is obtained by heating leucoquinizarin first with *p*-phenylenediamine and then with monoethanolamine in presence of boric acid and an oxidizing agent such as arsenic pentoxide or lead peroxide.

Another method for the synthesis of 1,4-diaminoanthraquinones unsymmetrically substituted on the two nitrogen atoms is to convert leucoquinizarin by mild ammonia treatment into leuco-1-amino-4-hydroxyanthraquinone, and without isolation add two other bases, e.g., methylamine and β-hydroxyethylamine, heat at about 90°, and oxidize with air and copper sulfate.[36]

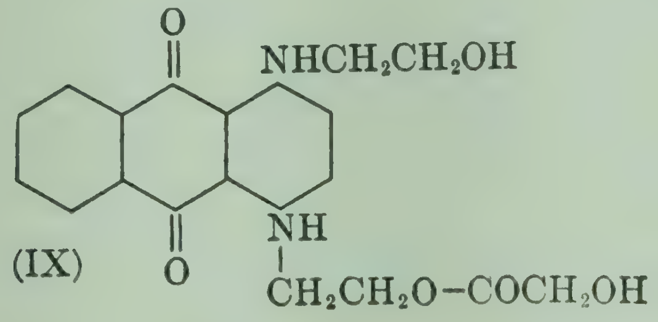
The treatment of primary or secondary amines with ethylene oxide or ethylene chlorohydrin, so that one or more β-hydroxyethyl groups are attached to the nitrogen atoms, is another method which is specially useful for compounds other than the 1,4-diaminoanthraquinone derivatives. Thus the hydroxyalkylation of diaminochrysazin gives a clear blue dye of high intensity.[37] The treatment of the green dye (VI) with ethylene chlorohydrin gives increased affinity for acetate silk.[38] The hydroxyethylation of 1,4,5-triamino-8-hydroxyanthraquinone gives blue dyes.[39] Similar dyes may be prepared from 1-amino-4-arylaminoanthraquinones with ethylene oxide or chlorohydrin, from 4-halogen-substituted 1-arylaminoanthraquinones by means of a hydroxyalkylamine, or from leuco-1,4-diaminoanthraquinone by condensation with a hydroxyalkylamine and an arylamine simultaneously or successively.[40] *m*-Hydroxymethylanilino groups may be introduced as in (VII).[41] Dyes of the type (VIII) dye both cellulose acetate and nylon.[42] Blue



(VII)



(VIII)



(IX)

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[36] British Celanese, BP 507,065; 507,206.

[37] IG, BP 430,658.

[38] IG, BP 275,636.

[39] Ciba, BP 391,859.

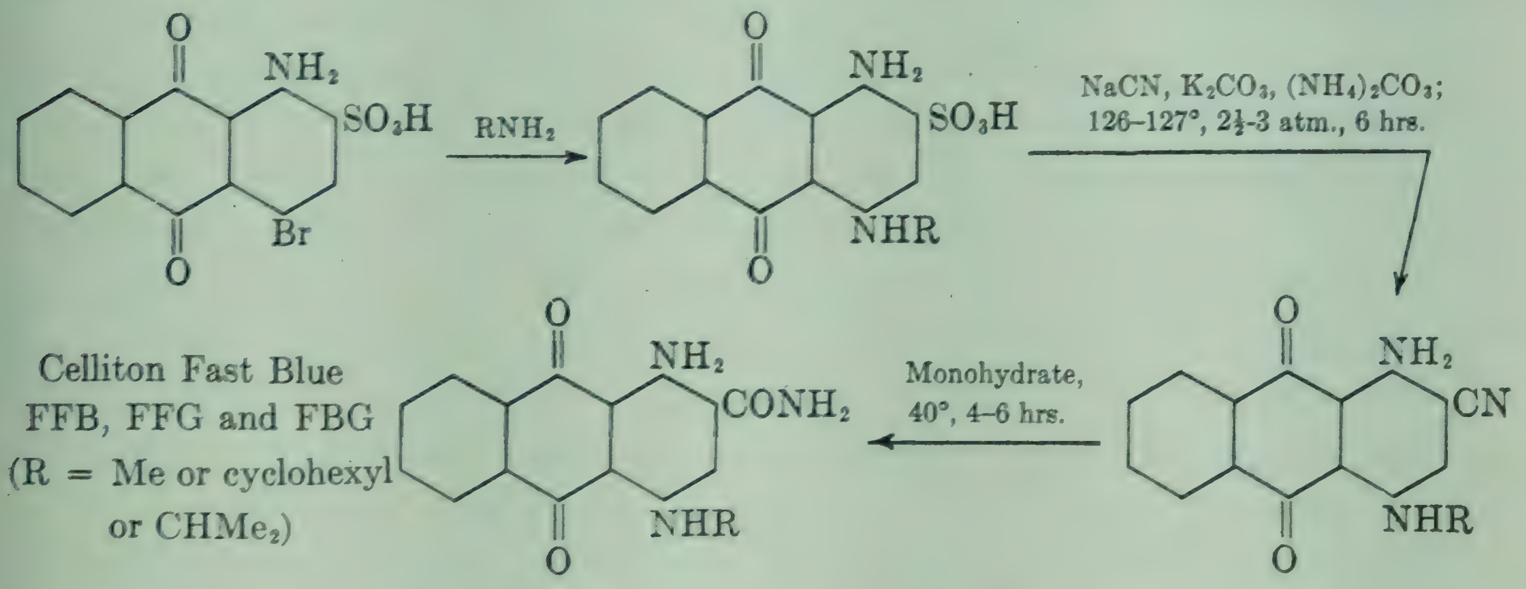
[40] Ciba, BP 425,517; GP Anm. J. 86,437; IG, BP 434,906.

[41] du Pont, BP 560,817.

[42] Byers, Dickey, and Eastman Kodak, BP 593,955; USP 2,391,011.

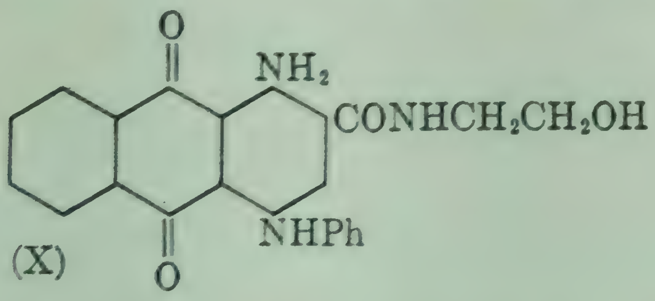
to green dyes (e.g. IX) are obtained by heating (III) with one mole of an acid chloride; for (IX), chloroacetyl chloride is used, and the chloroacetic ester is converted into the glycollic ester (IX) by means of boiling sodium carbonate solution.[43] Green-blue dyes are obtained by treating hydroxylamine derivatives, such as 4,8-bis-hydroxylaminoanthrarufin, with formaldehyde in alcoholic solution in presence of a copper salt.[44] Esters of suitably substituted anthraquinone-2-carboxylic acid and polyalkylene glycol monoalkyl ether, in which the number of carbon atoms in the aliphatic compound is less than 16, are cellulose acetate dyes; e.g., the 1-amino-2-anthraquinonyl ester of Cellosolve dyes an orange shade.[45]

Celliton Fast Blue FFB, FFG and FBG contain an amide group, and they are prepared from 4-bromo-1-aminoanthraquinone-2-sulfonic acid[30]


O
NH₂
SO₃H
Br
O
RNH₂
O
NH₂
SO₃H
NHR
O
NaCN, K₂CO₃, (NH₄)₂CO₃;
126–127°, 2½-3 atm., 6 hrs.
Celliton Fast Blue
FFB, FFG and FBG
(R = Me or cyclohexyl
or CHMe₂)
O
NH₂
CONH₂
NHR
O
Monohydrate,
40°, 4–6 hrs.
O
NH₂
CN
NHR
O

by the indicated series of reactions.[7] Celliton Fast Blue FFG is stated to be faster to light and gas fumes than the other Celliton blues.[46, 46a]

1-Amino-4-anilinoanthraquinone-2-carboxyl chloride and monoethanolamine give the blue dye (X), which is fast to light and gas fumes.[47]


O
NH₂
CONHCH₂CH₂OH
NHPh
O

(X)

Bright blue dyes for cellulose acetate are obtained by introducing one or more aliphatic polyethanoxyamine ether residues into the anthraquinone nucleus, or attached to the nitrogen in anthraquinonecarboxylic amides. Thus the amine NH_2–$(CH_2)_2$–O–$(CH_2)_2$–OMe is condensed with quinizarin, giving the 4-alkylamino-1-hydroxy- (violet) and the 1,4-dialkylaminoanthraquinone (bright blue).[48]

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[43] Dickey, McNally, and Eastman Kodak, USP 2,411,148.

[44] Seymour, Pull, and Celanese Corp. of America, USP 2,368,682.

[45] Slinger and ICI, BP 571,663.

[46] *FIAT* **1313,** III.

[46a] See also Olpin and House, USP 2,484,902.

[47] British Celanese, BP 518,725.

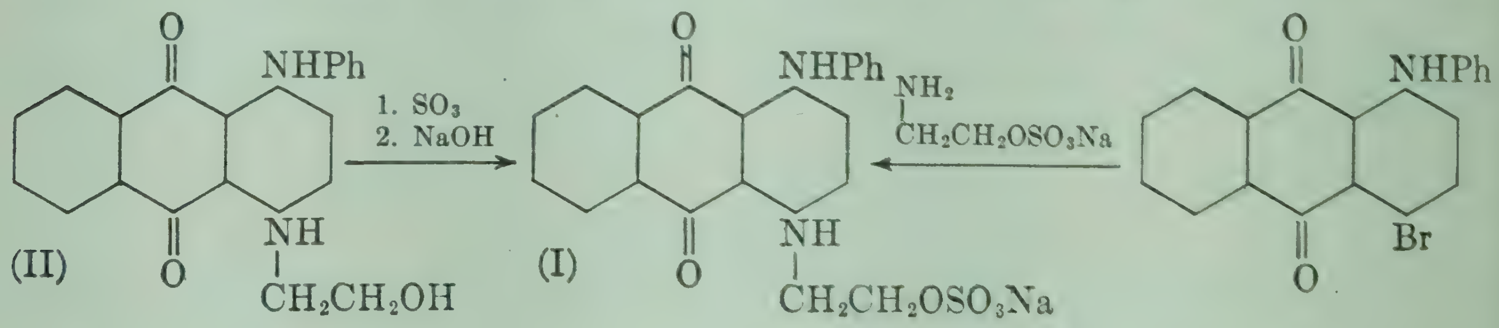
2-Bromo-1-amino-4-arylaminoanthraquinones (or the 2-sulfonic acids) give the 2-mercapto derivatives on heating with sodium hydrosulfide solution; condensation of the mercaptan with glycerol chlorohydrin gives a light-fast blue dye.[48a]

The condensation of chloroanthraquinones with phthalimide to form phthalimidoanthraquinones, of chloroanthraquinones with anthranilic acid, and of aminoanthraquinones with salicylic acid-5-sulfonyl chloride are other reactions which may be utilized for the present purpose.

WATER-SOLUBLE DYES

Solacet dyes. There is a complete analogy between the cellulose acetate dyes of the azo and anthraquinone series; in addition to aqueous dispersions of insoluble dyes of both the series, cellulose acetate dyes of the sulfuric ester type (Solacet dyes, ICI) have been prepared in the anthraquinone, as well as the azo series. The introduction of a sulfuric ester group renders the dyes water soluble, while the affinity required for application by the usual direct dyeing method is retained. The Solacets have excellent affinity for nylon and some are useful as wool dyes; the shades are somewhat less fast than on cellulose acetate, and some of the dyes exhibit different shades on cellulose acetate and on nylon.

A sulfuric ester of the type (I) may be prepared from the ethanolamine derivative (II) by the usual methods of sulfation with oleum or chlorosulfonic acid used in the preparation of wetting agents such as the sodium alkyl sulfates. Alternatively, 1-bromo-4-anilinoanthraquinone may be condensed with sodium β-aminoethyl sulfate.[49] Bright bluish violet dyes are produced by sulfating (with sulfuric acid or pyridine and alkali pyrosulfate) 1-aminoanthraquinones with halogen or methyl in the 2-position and the group $NH{-}CH(CH_2R){-}R'{-}OH$ in the 4-position; $R = H$ or alkyl and $R' =$ alkylene.[50] A sulfonic or phenoxy group in the 2-position may be replaced by heating with a dihydric alcohol



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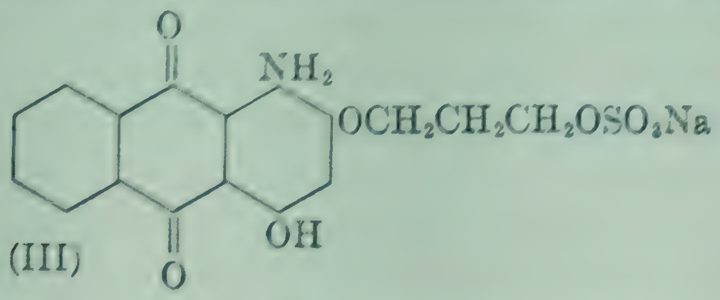
[48] ICI, BP 551,160.

[48a] Ciba, BP 607,955.

[49] Ciba, FP 849,793; Olpin and British Celanese, BP 285,641.

[50] ICI, BP 557,456.

and alkali. Thus, when 1-amino-4-hydroxy-2-phenoxyanthraquinone is heated with potassium hydroxide, trimethylene glycol and pyridine at 60°, the corresponding 2-γ-hydroxypropoxyanthraquinone is obtained; and treatment with 100% sulfuric acid at 15° gives the hydrogen sulfate, the sodium salt of which is a bright red dye (III) for wool and cellulose acetate.[51]



(III)

The discovery of the Solacet type has stimulated research on other modes of imparting solubility without prejudicing the affinity for cellulose acetate, and on the preparation of dyes which are of value for dyeing wool and nylon, as well as acetate rayon. Kodak describe a range of dyes solubilized by means of a sulfoalkylamino group, the alkyl group containing at least two carbon atoms;[52] examples are 1-amino-4-tetrahydrofurfurylaminoanthraquinones which carry the group $(CH_2)_nSO_3H$ attached to the 1-nitrogen.[53] The Ionamine type has been extended by using glucose and other hydroxyaliphatic aldehydes in place of formaldehyde for the aldehyde bisulfite reactions.[54]

Although the water-soluble dyes for cellulose acetate usually contain the solubilizing group in a side chain, the presence of a nuclear sulfonic group does not debar a dye from being useful for cellulose acetate. Acid colors of the Alizarin Direct Blue type (e.g., 1-amino-4-anilinoanthraquinone-2-sulfonic acid) become applicable to cellulose acetate if the phenyl nucleus contains a saturated hydrocarbon substituent (C_{3-6}), e.g., *n*-butyl.[55] When the anilino group is replaced by an aminoazobenzene residue the product dyes fast pure green shades;[56] when a *p*-nitroaniline is used a dyestuff is produced which builds up to black.[57] Sandoz describe a series of dyes of the usual 1,4-diarylaminoanthraquinone type, further substituted if desired, in which the 4-aryl group is of the type $o\text{-}C_6H_3R\text{–}NR'\text{–}Ac$, where R is methyl or ethyl, halogen, acylamido, carboxyl, or a carboxylic ester group, and R′ may be hydrogen, alkyl, or hydroxyalkyl; the products are prepared by heating a

[51] Buckley, Tatum, and ICI, BP 558,433.

[52] Eastman Kodak, USP 2,188,369.

[53] Eastman Kodak, USP 2,337,566.

[54] IG, FP 829,918.

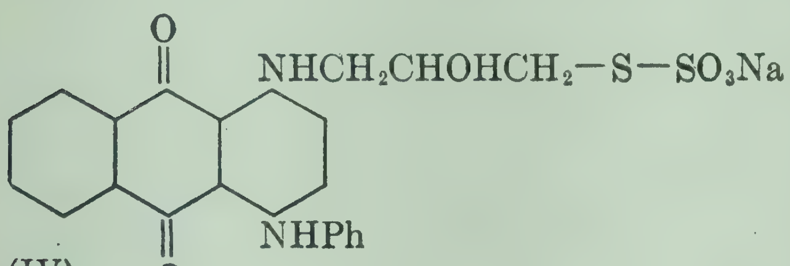
[55] Sharing, Slinger, Tatum, and ICI, BP 579,017.

[56] ICI, BP 478,665; 494,237.

[57] ICI, BP 507,748.

4-halogen derivative with the appropriate arylamine. The resulting product, if it still contains a halogen, for instance in the 2- or 5,8-positions, may be treated with sodium sulfite; or sulfonated. Blue dyes for wool and cellulose acetate are obtained. Examples of the arylamines used are 4,1,2-NH_2–C_6H_3Me–NHAc, –NH_2–C_6H_3Me–NMe–Ac, and 1,6,3-NHAc–C_6H_3Cl–NH_2.[58] Sulfonation of the products of the condensation of phenol, an aminoanthraquinone and formaldehyde gives cellulose acetate dyes.[58a]

The sulfuric esters (Indigosols; see Chapter XXXIV) of the leuco derivatives of vat dyes can be applied to cellulose acetate.[58b]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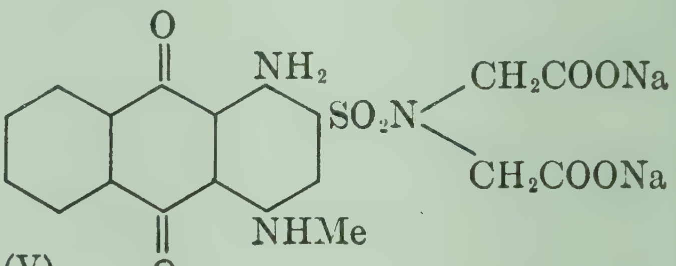
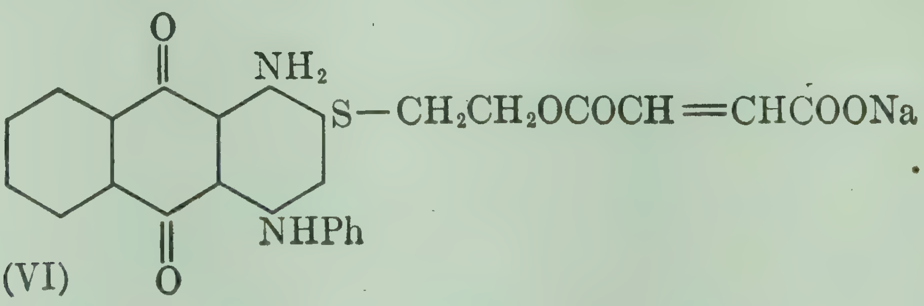

(V)

While the common solubilizing group is a sulfonic or sulfuric ester group, thiosulfate, sulfonamide, carboxyl, and other groups have also been suggested. The dyes (IV) and (V) are examples of these types;[59] the sulfonamide residue carries two carboxyl groups in (V), which dyes cellulose acetate and wool in level blue shades. ω-Hydroxyalkylaminoanthraquinones can be converted into water-soluble cellulose acetate dyes by heating with succinic or phthalic anhydride to form the acid esters, and neutralizing with sodium carbonate to form the sodium salts.[60] Carboxyl groups may be introduced by the addition of an α,β-unsaturated acid, such as acrylic acid, to an aminoanthraquinone.[61] Thioethers such as (VI) are water-soluble dyes for cellulose acetate.[62] The ethanolamine group confers partial solubility, and the solubility can


(VI)

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[58] Sandoz, BP 551,881.

[58a] Sandoz, SP 224,874–9.

[58b] Textron Inc., BP 633,717.

[59] IG, BP 490,945; Ciba, BP 510,453; IG, BP 496,126.

[60] ICI, BP 506,526; Tatum and ICI, USP 2,329,798; see also Grossmann and Ciba, USP 2,392,663.

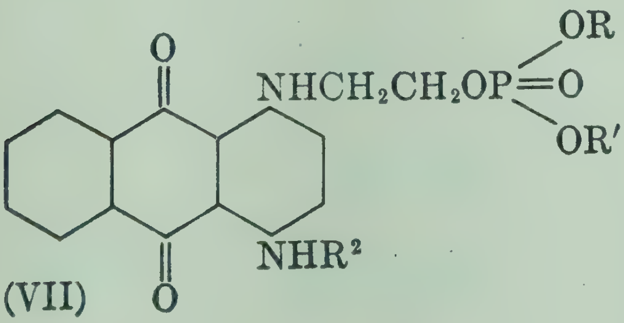
[61] IG, BP 478,304.

[62] Grossmann and Ciba, USP 2,441,355.

be increased by extending the alcohol chain by means of ether linkages. Thus leucoquinizarin may be condensed with β-aminoethyl β′-hydroxyethyl ether to yield 1-hydroxy-4-alkylamino or 1,4-dialkylaminoanthraquinones; or suitable negatively substituted anthraquinones may be condensed with di- or tetra-ethylene glycol ethers, yielding soluble dyes of blue and green shades.[63] Water-soluble dyes in which the solubilization is effected by the requisite number of hydroxyl, carboxyl and ester groups may be used. Anthraquinone derivatives, having not less than two amino groups and also the group –NH–X–O–CO–Y–COONa, where X is alkylene and Y is the same or arylene, are water-soluble, and are fast violet to blue-green dyes for cellulose acetate. The method of preparation is to condense tri- or tetraminoanthraquinones or their leuco derivatives with one mole of an appropriate halogenoalkyl or glycidyl ester, or with an amine NH_2–X–O–CO–Y–CO_2H, or to esterify the appropriate hydroxy- or halogeno-alkylaminoanthraquinone with a di- or polycarboxylic acid. As examples, 1,4,5,8-tetraminoanthraquinone is condensed with acid β-chloroethyl succinate or maleate in cresol solution, giving a blue dye, while 1,4,5-triamino-8-*p*-aminoanilinoanthraquinone gives, with acid γ-chloro-β-hydroxypropyl succinate, a blue-green dye.[64] Tri or tetraminoanthraquinones can be solubilized by condensation with a monohalogenoacetic acid in phenol solution or with phthalic anhydride in nitrobenzene, isolating the products as the alkali salts.[65]

Water-soluble quaternary salts may be employed; the pyridinium salt obtained from 1-β-chloroethylamino-4-anilinoanthraquinone dyes acetate rayon in greenish blue shades.[66]

Aminoanthraquinones may be converted into phosphoric acid derivatives of various types; the treatment of a hydroxyalkylaminoanthraquinone or an aminoanthraquinone itself (e.g. 1,4-diamino-2-methoxyanthraquinone) with phosphorus oxychloride gives water-soluble dyes.[67] Phosphoric esters of the type of (VII) are suitable.[68]



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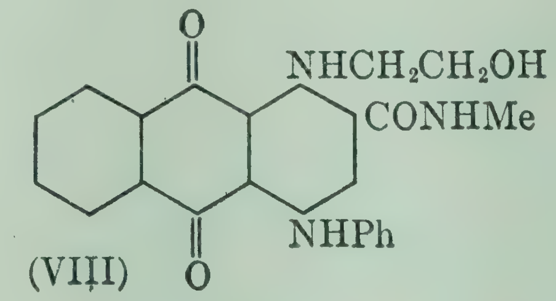

(VIII)

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[63] IG, BP 512,483.

[64] Ciba, BP 545,251.

[65] Ciba, BP 546,019; SP 227,585; 230,214–7.

[66] ICI, BP 481,942.

[67] IG, BP 455,092; 487,878.

[68] Eastman Kodak, USP 2,326,047.

Gas Fading

Some cellulose acetate dyes, especially anthraquinone derivatives, are susceptible to fading on prolonged exposure to the fumes of burning coal gas. Nitrogen oxides in the fumes diazotize the amino groups, resulting in the formation of nitrosamines; sulfur dioxide in the fumes plays no essential part.[69] For test purposes, gas fading can be accelerated by the use of nitrogen oxides at high concentration; a temperature of 55° and RH 15% are suitable for a standard accelerated test procedure.[70] Gas fading depends on the constitution of the dyes, and some examples of dyes claimed to be resistant to gas fading have been cited earlier. Recent patent literature discloses a special search for blue dyes with high resistance to gas fading. 1,4-Diaminoanthraquinone and its derivatives carrying a trifluoromethyl group in the 2-position have good gas and light fastness.[70a] In dyes of the type 1-alkylamino-4-arylaminoanthraquinone, the light fastness is increased by 200–300% and the stability to gas fading by 100% if the aryl group is a complex group such as p-$C_6H_4OC_2H_4OC_2H_4OC_2H_4OMe$.[70b] The dyes (VIII) represent a simple type for which fastness to gas fading is claimed.[71] 1-Hydroxyanthraquinones substituted in the 4-position by –NH–Ar–CH_2X, in which X is CN, NHAr or OMe, are blue dyes fast to gas fumes; CH_2X may be replaced by OCH_2COOH or OCH_2CH_2OH.[72] When 1-amino-4-butylaminoanthraquinone-2-carboxylic acid is heated with aqueous sodium cyanide and bicarbonate, the product is the 3-cyano compound; such blue dyes have improved resistance to gas fading.[73] When 1-hydroxy-4-butylaminoanthraquinone-2-sulfonic acid is heated with aqueous sodium cyanide, the product is the 2,3-dicyano derivative, which dyes cellulose acetate a fast reddish blue shade highly resistant to acid fading.[73a] Blue dyes fast to burnt gas fumes are obtained by reducing 4,8-dinitro-1,5-dihydroxyanthraquinone with alkaline stannous chloride to the bishydroxylamine derivative, and condensing the latter with an aldehyde.[74] Certain anthrapyridone derivatives, such as 1-acetyl-6-*o*-toluidinoanthrapyridone-4-sulfonic acid, dye cellulose acetate in red and red-violet shades which are "extremely fast to light and resistant to acid fading."[74a] Since azo and anthraquinone dyes have relatively better fastness to fumes and light respectively, a compromise between the two requirements can be achieved by using a mixture of an azo dye and an anthraquinone dye. With a given dye, gas fading can be minimized by treatment of the dyed material with sodium thiosulfate,[75] triethanolamine,[76] N-β-hydroxyethyl ethylenediamine in alcohol,[77] N,N'-diphenylethylenediamines,[78] cyanamide,[79] melamine and melamine-formaldehyde resins.[80] The fastness to burnt gas fumes of acetate rayon dyed with azo or anthraquinone dyes is improved by treatment of the fiber, during or after dyeing, with reagents of the type of 1,6-dianilinohexane.[81] Duranol Inhibitor GF (ICI) is such a protective agent, which is attacked preferentially by the reactive constituents of the atmosphere.[82]

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[69] Rowe and Chamberlain, *J. Soc. Dyers Colourists* **53,** 268 (1937).

[70] Ray *et al., Am. Dyestuff Reptr.* **37,** 529 (1948).

[70a] Eastman Kodak, USP 2,451,478. See also USP 2,487,045; 2,466,008–9.

[70b] Eastman Kodak, USP 2,459,149.

[71] Olpin and House, BP 603,880.

[72] du Pont, USP 2,335,680; 2,333,384.

[73] British Celanese, BP 593,485; 639,587.

[73a] Seymour *et al.,* USP 2,445,007; 2,496,414; British Celanese, BP 614,969.

[74] British Celanese, BP 552,141.

[74a] British Celanese, BP 613,319.

[75] Bunbury, Giles, and ICI, BP 460,027.

[76] British Celanese, BP 571,677.

[77] British Celanese, BP 612,601.

[78] Collie, Giles, Wilkinson, and ICI, USP 2,416,380.

[79] Bonard, USP 2,440,330; Dreyfus, BP 571,056.

[80] Eastman Kodak, USP 2,176,506; British Celanese, 2,403,019.

[81] ICI, BP 558,784.

[82] Knight, *J. Soc. Dyers Colourists* **66**, 171 (1950).

Chapter XXVIII

ANTHRAQUINONE MORDANT DYES

Among the many hydroxyanthraquinones which have been isolated from nature or synthesized, Alizarin[1] is the only one which is of major technical importance at the present time as a dye, but several are of value for modifying the Alizarin shades by admixture and as intermediates for the preparation of acid colors of the anthraquinone series.

Alizarin

Alizarin[2] (Robiquet and Colin, 1826; CI 1027) occurs as the 2-primeveroside,[3] ruberythric acid, in the root of the madder plant (*Rubia tinctorum* and other *Rubia* species), cultivated and used as a coloring matter for many centuries. Graebe and Liebermann determined the constitution of Alizarin as 1,2-dihydroxyanthraquinone and synthesized it in 1868. Their first synthesis from dibromoanthraquinone was replaced within a year by the technically feasible process of sulfonating anthraquinone and fusing the product with alkali, patented on two successive days by Caro, Graebe and Liebermann and by Perkin. This artificial Alizarin produced commercially was however a mixture of Alizarin, Flavopurpurin (1,2,6-trihydroxyanthraquinone) and Anthrapurpurin (1,2,7-trihydroxyanthraquinone). Further work showed that Alizarin was not formed from anthraquinone disulfonic acid, but from the β-monosulfonic acid, and that the disulfonic acid formed in the sulfonation led to the trihydroxy compounds. It then became apparent that in the alkali fusion of an anthraquinone sulfonic acid, as distinct from similar reactions in the benzene and naphthalene series, an additional hydroxyl group is introduced by oxidation, and Koch discovered that the yield of Alizarin is considerably improved by the addition of an oxidizing agent. Synthetic Alizarin is now manufactured[4] by heating sodium anthraquinone-β-sulfonate ("silver salt") with aqueous caustic soda and sodium nitrate (or chlorate) in an autoclave at 200°; the product is the soluble disodium salt, and Alizarin is precipitated by acidification. The IG process for the manufacture of Alizarin is to heat silver salt free from disulfonic acid (2400 kg.) with 49% caustic soda solution (3200 kg.) and sodium nitrate (400 kg.) at 190–200° (10 atms. pressure) in a horizontal autoclave for 10 hours. Alizarin is then isolated by diluting the batch with water, adding salt and acidifying to pH 2. The yield is 1750 kg. Alizarin Red B paste as 100%. Alizarin Red F is prepared similarly from Silver Salt F, a less pure substance than Silver Salt B used for Alizarin Red B.[5]

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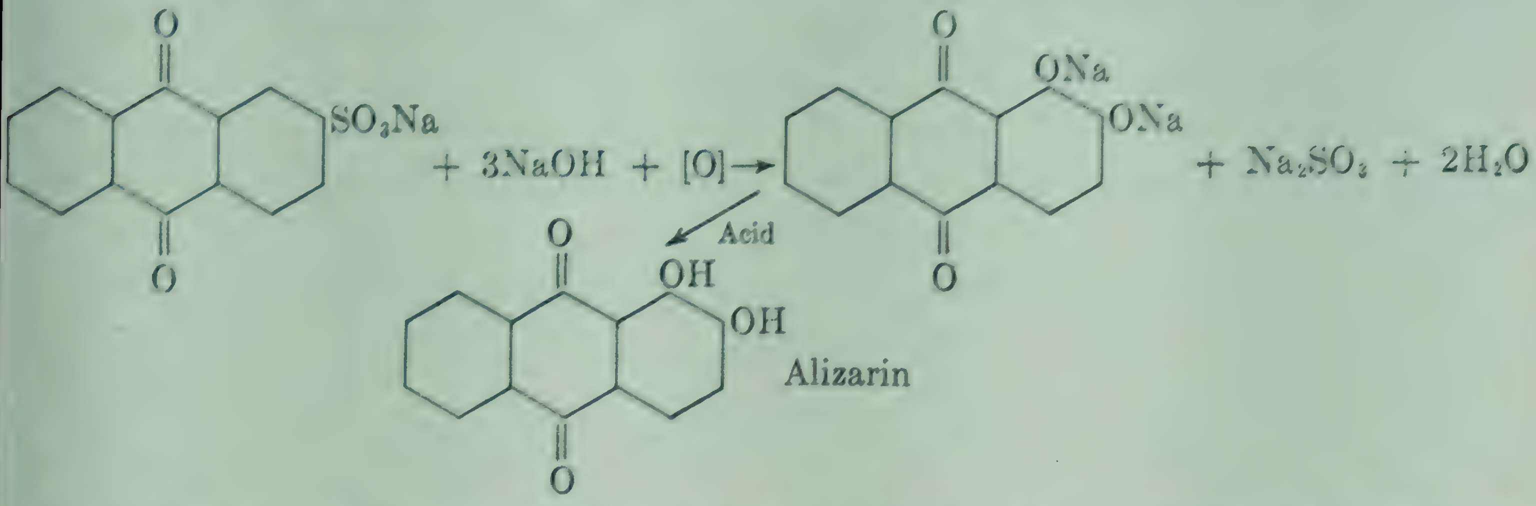
[1] See Richter in Thorpe's Dictionary of Applied Chemistry, 1, Longmans, London, 1937, p. 203.

[2] For an account of the history of Alizarin, its industrial and economic importance, see Wahl, *Bull. soc. chim.* (4) **41**, 943 (1927); Fieser, *J. Chem. Education* **7**, 2609 (1930).

[3] Richter, *JCS* 1701 (**1936**); Zemplen, *Math. naturw. Anz. ungar. Akad. Wiss.* **58**, 380 (1939).

[4] Ullmann, Enzyklopädie der technischen Chemie, 2nd ed., 1, Urban and Schwarzenberg, Berlin, 1928, p. 197.



The pure monosulfonate is necessary for the production of Alizarin free from trihydroxy compounds, and some anthraquinone has to be left unsulfonated so as to avoid disulfonation; but in a process due to Iljinsky,[6] the sulfonation is completed and the mixture of mono- and disulfonic acids submitted to alkali fusion. Alizarin is then separated from Flavopurpurin and Anthrapurpurin through their calcium salts. Sublimation is a convenient method for purifying Alizarin and other hydroxyanthraquinones in the laboratory. Alizarin sublimes at 110°, while Flavopurpurin and Anthrapurpurin sublime at 160° and 170°, and by sublimation at 140° Alizarin may be estimated in admixture with these trihydroxyanthraquinones.

An interesting method of preparing Alizarin, which is claimed to be in very pure form free from isomers, is to heat anthraquinone with potassium hydroxide, sodium chlorate, and water at 200° in an open vessel or an autoclave until no more oxidizing agent remains.[7] The production of Alizarin in 90–93% yield by heating anthraquinone, caustic soda solution, sodium sulfite and calcium nitrate in an autoclave at 220–225° has been claimed.[8]

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[5] *BIOS* **1484.**

[6] Wedekind and Co., DRP 140,127–9; 194,955.

[7] BASF, DRP 186,526.

[8] Il'inskii *et al.*, *Org. Chem. Ind. U.S.S.R.* **2**, 9 (1936).

Alizarin cystallizes from alcohol in brilliant brownish-yellow needles, and sublimes in orange-red needles, m.p. 290°, b.p. 430°; it is readily soluble in the common organic solvents; it dissolves in aqueous caustic soda with a purple color. Alizarin is a typical mordant dye, insoluble in water, and is sold as a 20% paste. While it is a polygenetic dye, giving different shades with different mordants (rose-red on aluminum, red-violet on tin, brown-violet on chromium and violet-black on iron), its use in dyeing and printing is for the production of the well-known Turkey Red on an alum mordant. Pure Alizarin yields a bluish red, and for yellower shades Alizarin is admixed with Purpurin, Anthrapurpurin or Flavopurpurin. Turkey Red dyeing is a tedious process, involving a series of prolonged treatments of oiling (formerly with rancid olive oil and now with Turkey Red oil), mordanting with aluminum sulfate and chalk, fixing, dyeing, steaming, and soaping. Turkey Red is prized for the beauty of the shade and its high fastness, and is still used for dyeing cotton yarn and for calico printing, especially in India; but it is slowly giving way to the azoic reds which are much simpler to produce.

Alizarin lakes may be prepared in substance, for use in paints, printing inks, and similar products, by dissolving Alizarin in caustic soda solution and treating with Turkey Red oil, sodium sulfite, aluminum acetate and calcium acetate solution at the boil. By varying the conditions of treatment, lakes of different overtone, undertone, texture and oil absorption capacity can be prepared.[9] Other anthraquinone mordant and acid dyes are also useful in lake making.

Turkey Red contains both aluminum and calcium as part of the lake produced on the fiber. The composition varies with the dyeing process, and varied structures have therefore been suggested for the Alizarin-aluminum-calcium complex. Bancroft has made a phase rule study of the reaction between Alizarin and alumina, and he regards the lakes as adsorption complexes.[10] The fatty acid used in Turkey Red dyeing acts as a dispersing agent for the complex calcium-aluminum alizarate and is not a constituent of the complex itself.[11, 12] Fierz-David and Rutishauser[12] regard Turkey Red lake as a well-defined compound, isolable in pure form by suitable treatment and containing Alizarin, aluminum and calcium in the proportions 4:2:3. The lake crystallizes from pyridine as a pyridine complex. Formula (I) has been suggested for the true Turkey Red lake, which contains 5 moles of water.[12] The structure of the lake requires further investigation, although there is little doubt that

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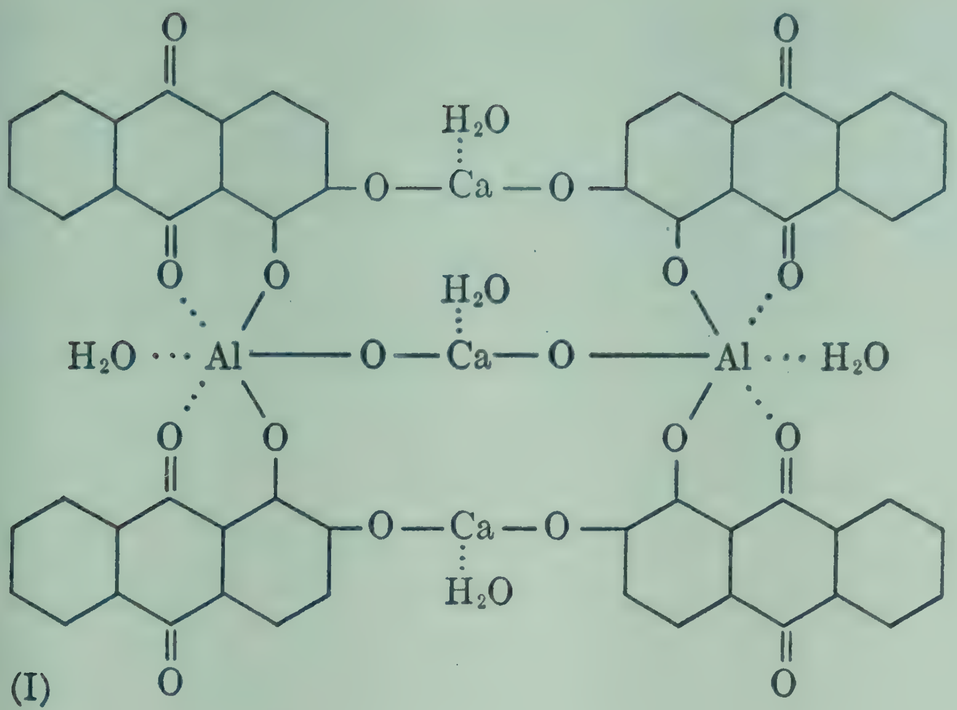
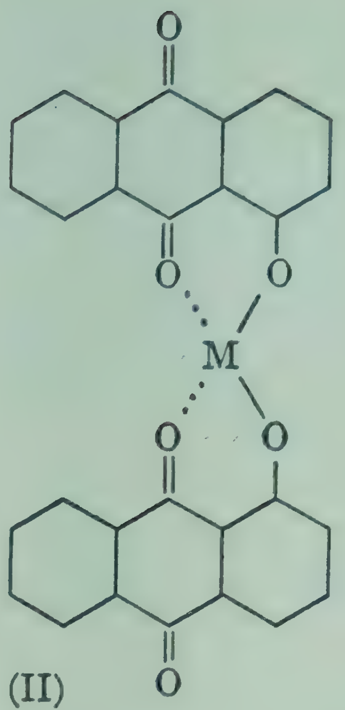
[9] Yates, *Ind. Chemist.* **18,** 348 (1942).

[10] *J. Phys. Chem.* **36,** 3137 (1932); and earlier papers.

[11] Haller, *Kolloid Z.* **13,** 263 (1913); *Helv. Chim. Acta* **23,** 1529 (1940); *J. Soc. Dyers Colourists* **58,** 141 (1942).

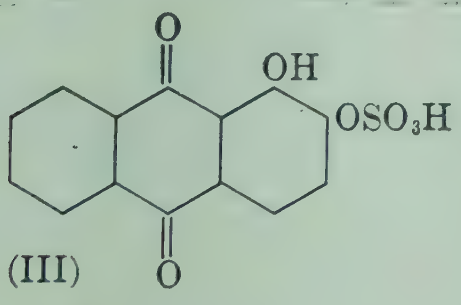
[12] *Helv. Chim. Acta* **23,** 1298 (1940).


(I)


(II)

aluminum is held in a chelate complex between the 1-hydroxyl and the adjacent carbonyl group, and the 2-hydroxyl group forms a salt with calcium; calcium may be replaced by other metallic radicals including aluminum. Geyer and Smith[13] have prepared cobalt, copper and other complexes of 1-hydroxyanthraquinone and the copper complex of 2-acetylalizarin, and have adduced analytical and spectral evidence to show that inner or chelate complexes of the type (II) are formed in the case of, for instance, four-coordinate cobalt, nickel and copper.

Derivatives of Alizarin. An interesting derivative of Alizarin is the β-sulfuric ester (III), prepared by the action of sulfur trioxide and pyridine. The compound is stated to yield prints fast to rubbing when applied on cotton in conjunction with aluminum sulfate and calcium acetate.[14] The β-hydroxyl group undergoes the usual reactions more readily than the α- because of the chelation of the latter with the neighboring carbonyl group, but di-*o*-derivatives (e.g., the dimethyl ether) can be prepared under suitable conditions. Alizarin forms the 3-bromo compound on bromination,[15] but the 2-methyl ether gives the 4-bromo compound. 4-Chloro- and 4-bromoalizarin can be prepared by halogenating alizarin-2-*p*-toluenesulfonate to (IV) and subsequently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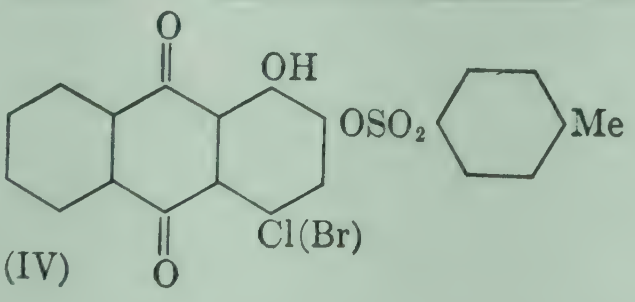
(IV)

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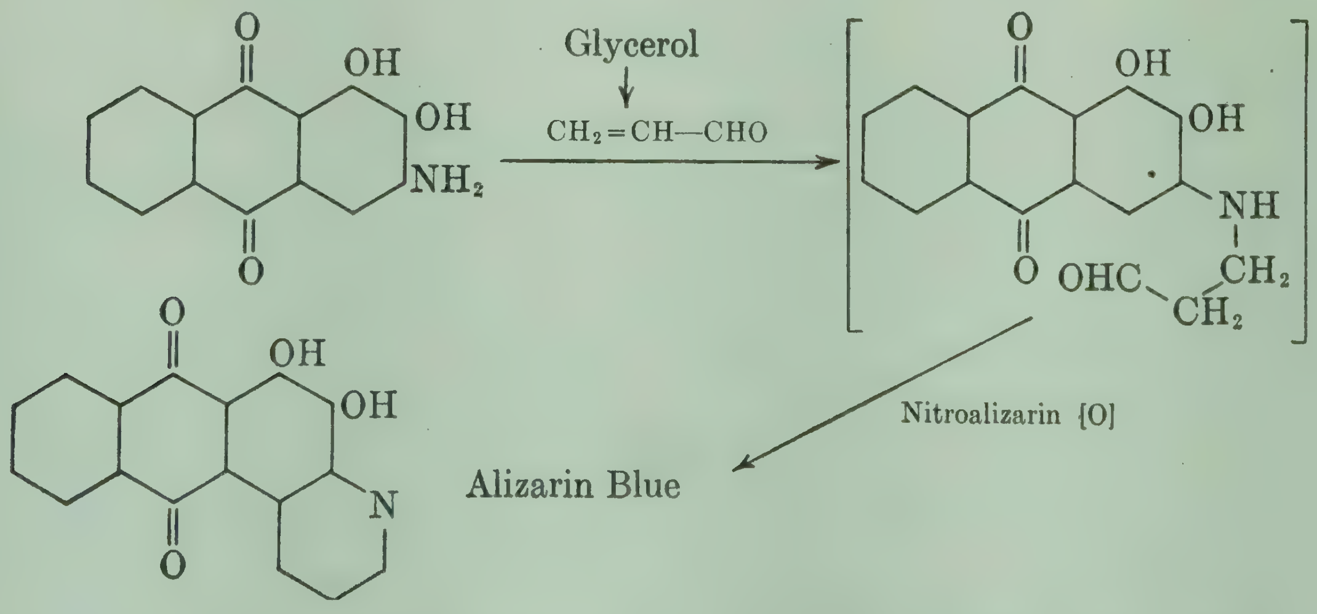
[13] *JACS* **64**, 1649 (1942).

[14] Barnes, Service, Thomas, and Scottish Dyes, BP 358,465.

[15] Perkin, *JCS* **27**, 401 (1874); Perkin and Haddock, *ibid.* 1512 (**1933**); Dimroth, Schultze, and Heinze, *Ber.* **54**, 3035 (1921).

hydrolysing the *p*-toluenesulfonyl group by means of sulfuric acid.[16] Alizarin is unaffected by iodine in boiling pyridine, by which treatment β-hydroxyanthraquinone gives a nearly quantitative yield of the 3-iodo compound.[17] 3-Iodoalizarin was first prepared by treating alizarin-1-methyl ether with iodine in pyridine and then demethylating with hydrobromic acid;[17] and more recently from 3-aminoalizarin dimethyl ether by the Sandmeyer reaction and subsequent demethylation.[17a] The interest in 3-iodoalizarin is its opacity to X-rays in connection with biological studies.[17a] 4-Iodoalizarin, which may also be of use in X-ray visualization, has been prepared by the Sandmeyer reaction on 4-aminoalizarin-2-methyl ether and demethylation with aluminum chloride.[16]

Nitration of Alizarin gives the 3- or 4-nitro compound according to the conditions of nitration. 3-Nitroalizarin (Alizarin Orange) (Rosenstiehl, 1876; CI 1033) (orange-yellow needles, m.p. 244° dec.), formed by nitration in concentrated sulfuric acid in presence of boric acid or with 62% nitric acid in *o*-dichlorobenzene at 40°,[5] has a limited use for orange shades on aluminum mordant. 4-Nitroalizarin (Perkin, 1876; CI 1031) (brownish yellow needles, m.p. 289° dec.) is obtained by nitrating Alizarin in sulfuric acid or oleum at −5° to −10°; it is best prepared by nitration of alizarin dibenzoate, followed by alkaline hydrolysis. Reduction of the α- and the crude β-nitro compounds with sodium sulfide gives the amines, Alizarin Garnet R (MLB; CI 1032) and Alizarin Maroon (B; CI 1041), which are now obsolete as dyes; the latter was largely 3-amino-1,2,4-trihydroxyanthraquinone. Prud'homme (1877) observed that the action of concentrated sulfuric acid on glycerine solutions of Alizarin and β-nitroalizarin (prepared for calico printing) gave a blue dye with mordant dyeing as well as weakly basic properties. Brunck (1881) prepared the dye, Alizarin Blue (CI 1066), in pure form, and Graebe elucidated its constitution as a pyridine derivative and the probable



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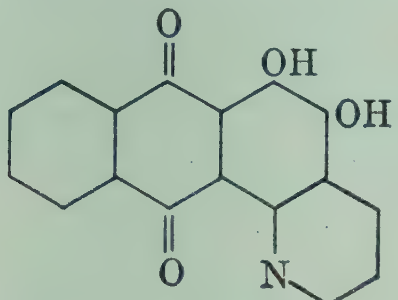
[16] Joshi, Tilak and Venkataraman, *Proc. Indian Acad. Sci.* **34A,** 304 (1951).

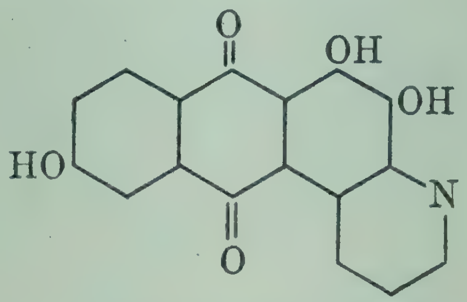
[17] Perkin and Story, *JCS* 2620 (**1931**).

[17a] Pratt and Archer, *JACS* **71,** 2938 (1949).

mechanism of the reaction. The Skraup synthesis of quinoline (from aniline, nitrobenzene, glycerol and concentrated sulfuric acid) was developed from this reaction. Alizarin Blue is now prepared by heating a mixture of 3-nitro and 3-aminoalizarin with glycerol and 83% sulfuric acid at 110° for 3 hours. Like Alizarin, Alizarin Blue is an insoluble mordant dye, and for calico printing the soluble bisulfite compound Alizarin Blue S (B; CI 1067) is used. An isomer of Alizarin Blue, prepared by carrying out the Skraup reaction on 4-aminoalizarin, is Alizarin Green (S Paste is the bisulfite compound; CI 1068). 3-Aminoflavopurpurin similarly yields Alizarin Black P (MLB; CI 1069), the bisulfite compound being marketed as Alizarin Black S (CI 1070).

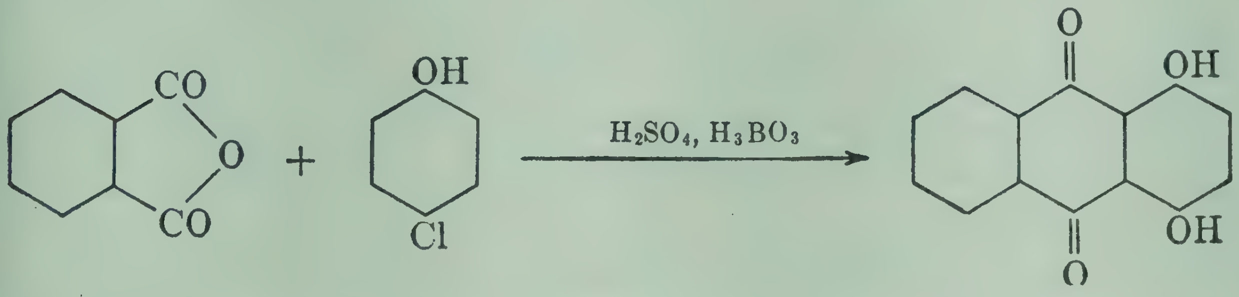


Alizarin Green



Alizarin Black P

Other dihydroxyanthraquinones. All the nine isomers of Alizarin are known; none is useful as a dye, but the 1,4-, 1,5- and 1,8-compounds, especially the first, are valuable intermediates. Quinizarin (Grimon, 1873; CI 1028) is manufactured on a large scale in connection with the production of acetate silk dyes and acid dyes of the type of Alizarin Cyanine Green and Alizarin Irisol; a convenient method is by the action of phthalic anhydride on *p*-chlorophenol in presence of sulfuric acid and boric acid.[18] IG have found that this reaction can be carried out in the absence of boric acid, and also by using aluminum chloride instead of sulfuric and boric acids.[19] An interesting suggestion is the use of diazotized *p*-chloroaniline in this reaction in place of *p*-chlorophenol.[20] Quinizarin is also formed by the Bohn-Schmidt reaction (*vide infra*) taking place when anthraquinone is oxidized by fuming sulfuric acid in presence of sodium nitrite and boric acid under specified conditions.[21] Electro-



Quinizarin

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[18] Bigelow and Reynolds, *OSCV* I, p. 476. See also Sievenpiper and Allied Chemical and Dyestuff, USP 2,445,538.

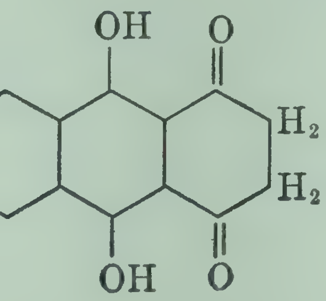
[19] *BIOS* **987.**

[20] Gubelmann, Weiland, and Newport Chem. Corp., USP 1,790,915.

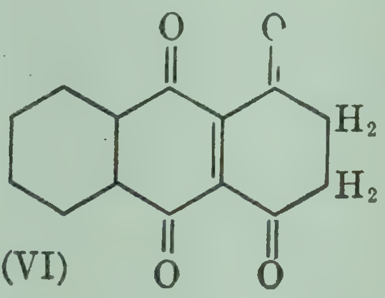
[21] Schmidt, *Bull. soc. ind. Mulhouse* **84,** 409 (1914).

chemical oxidation of anthraquinone to Quinizarin is a further method.[22] A synthesis which has a bearing on the constitution of Quinizarin is the condensation of maleic anhydride with 1,4-dihydroxynaphthalene in presence of sodium chloride-aluminum chloride at 220°.[23] 5-Chloroquinizarin is obtained by heating 5-chloro-1-nitro or 5-chloro-1-aminoanthraquinone with sulfuric acid in presence of boric acid and sodium nitrite at 150–220°.[24]

The value of Quinizarin as an intermediate is its reactivity, especially in its leuco form. By heating the latter with an arylamine such as *p*-toluidine, one or both the hydroxyl groups in Quinizarin may be replaced by the arylamino group.[25] Zahn and Ochwat have shown[23] that leucoquinizarin probably has the constitution (V), and that by careful oxidation this may be converted into dihydroquinizarinquinone (VI), isomeric with quinizarin.[26] The new quinone reacts with aromatic amines to give, for instance, 1-*p*-toluidino-4-hydroxyanthraquinone. The reactivity of Quinizarin may be utilized for the preparation of various other anthraquinone derivatives. On boiling an aqueous mixture of quinizarin, sodium sulfite and copper oxide, the sodium salt of the 2-sulfonic acid is obtained in theoretical yield; 1,4,5,8-tetrahydroxyanthraquinone is unreactive under the same conditions.[27] Quinizarin (or better sodium quinizarin-2-sulfonate) gives with potassium cyanide 2,3-dicyanoquinizarin, which may be hydrolyzed to the dicarboxylic acid. This acid undergoes the usual *o*-dicarboxylic acid reactions, such as condensation with aromatic hydrocarbons.[28]



(V)



(VI)

The condensation of *m*-hydroxybenzoic acid with itself, or heating anthraquinone-1,5-disulfonic acid with milk of lime under pressure, leads to the corresponding dihydroxy compound, Anthrarufin (Schunck and Roemer, 1878; CI 1029). Chrysazin (Liebermann, 1876; CI 1030) is similarly prepared from the 1,8-disulfonic acid. Suitable conditions for such hydroxylation are to use the potassium salt of the disulfonic acid, water, chalk and magnesium chloride and to heat at 215° for a few hours.[5]

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[22] Rasch and Lowy, *Trans. Electrochem. Soc.* **62** (preprint), 8 (1932).

[23] Zahn and Ochwat, *Ann.* **462,** 72 (1928).

[24] Lulek, Buxbaum, and du Pont, USP 2,346,772.

[25] See Chapter XXIX.

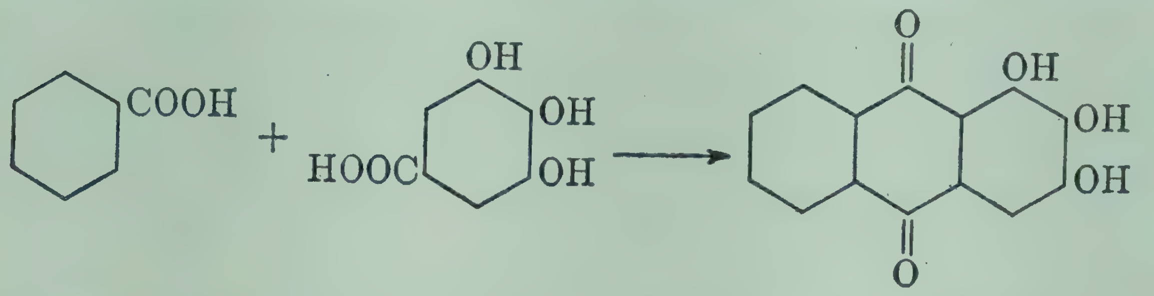
[26] See also Green, *JCS* 1428 (**1926**); IG, BP 380,062.

[27] Marshall, *JCS* 3206 (**1931**).

[28] Marschalk, *Bull. soc. chim.* (5), **2,** 1809 (1935); (5) **4,** 184 (1937).

Trihydroxyanthraquinones

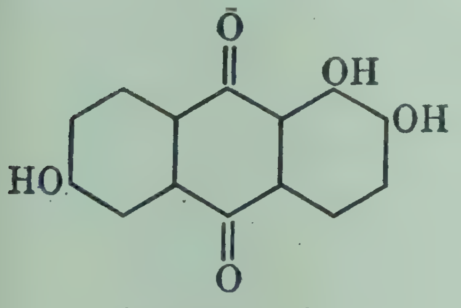
The hydroxy derivatives of Alizarin are important. Anthragallol (CI 1035) is obtained by heating a mixture of benzoic acid and gallic acid with a mixture of monohydrate and oleum at 120°; but at the same time some of the gallic acid condenses with itself with the formation of the hexahydroxy compound, Rufigallic acid (Rufigallol; CI 1052). This is not undesirable as the latter improves the shade. Anthragallol is of some practical interest as it gives a fast brown on chromium mordant. A mixture of Anthragallol and Rufigallol is marketed as Alizarin Brown HD (IG).



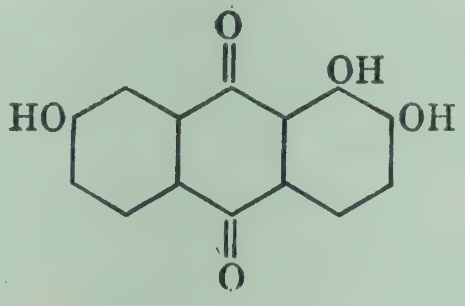
Anthragallol

Oxidation of Alizarin with manganese dioxide and sulfuric acid (Bohn-Schmidt reaction) gives Purpurin (1,2,4-trihydroxyanthraquinone) (CI 1037), which gives a scarlet on aluminum mordant and is a useful intermediate for the preparation of acid-mordant dyes.[25] Purpurin may also be synthesized by heating sodium quinizarin-2-sulfonate with slaked lime and water in an autoclave at 250°.[27]

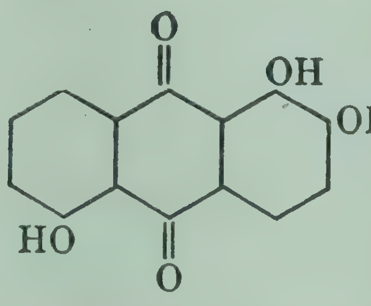
Flavopurpurin (CI 1039) and Anthrapurpurin (CI 1040) are made from anthraquinone-2,6- and 2,7-disulfonic acids in the same manner as Alizarin from the β-monosulfonic acid. Fusion of Anthrarufin with potassium hydroxide or treatment of Alizarin with sulfuric acid and boric acid leads to Brilliant Alizarin Bordeaux R (By) (CI 1038). These trihydroxyanthraquinones are made in the pure state for mixing with Alizarin for shading purposes.



Flavopurpurin



Anthrapurpurin

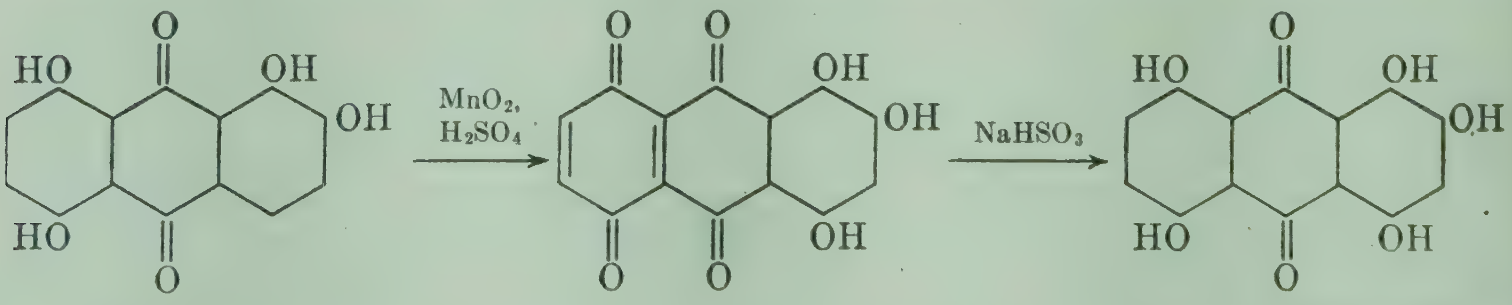


Brilliant Alizarin Bordeaux R

Polyhydroxyanthraquinones

In attempting the sulfonation of Alizarin Blue, Bohn (1888) made the important observation that anthraquinone and its derivatives can be directly hydroxylated by the action of fuming sulfuric acid at a moderate temperature. Three hydroxyl groups could be thus introduced into Alizarin Blue, the bisulfite compound being marketed as Alizarin Indigo Blue S (BASF; CI 1072) for dyeing wool on a chromium mordant. The usual result is to introduce two hydroxyl groups *para* to each other in the unsubstituted ring, so far as this is possible. Anthraquinone itself yields Quinizarin in this manner, but the method is more valuable for the further hydroxylation of hydroxyanthraquinones and for the preparation of the tetra-, penta- and hexahydroxyanthraquinones. Schmidt (By) discovered the reaction independently, and made the even more important observations that traces of selenium or mercury, often present in commercial sulfuric acid, are powerful catalysts, and that boric acid has a profound effect in moderating and controlling the course of the reaction. Various experimental modifications of the Bohn-Schmidt reaction have since been made, of which the following are a few examples.

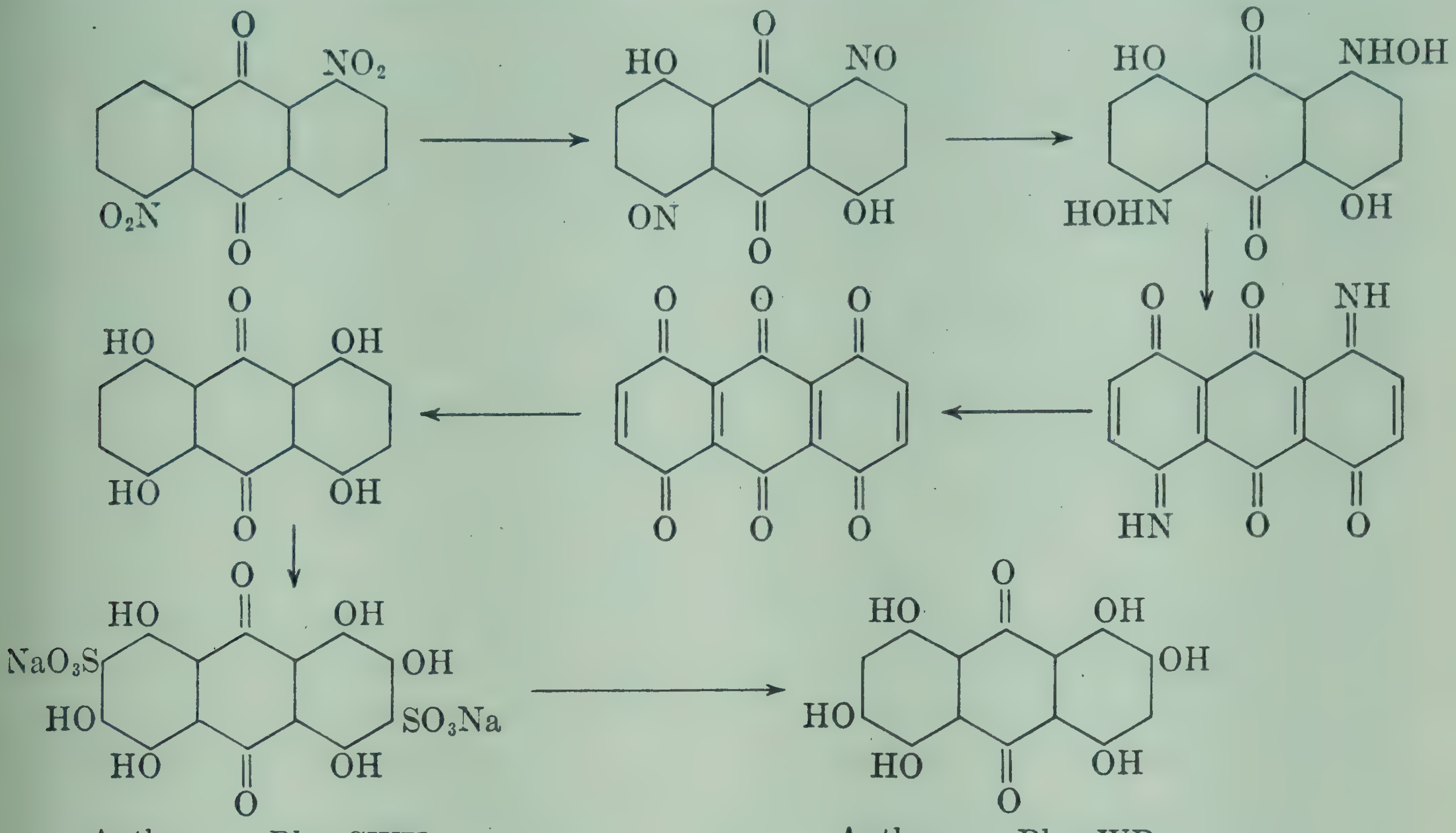
(1) When Alizarin is treated with 80% fuming sulfuric acid at 30°, it is not sulfonated, but two hydroxyl groups are added, giving Alizarin Bordeaux B or Quinalizarin (Schmidt, 1890; CI 1045), which dyes a bordeaux on aluminum mordant. The primary products of the reaction appear to be sulfuric esters which are then hydrolyzed to the hydroxy compounds. The addition of boric acid retards and regulates the reaction by forming boric esters (AQ–OB=O), as well as chelate compounds of boron in association with the α-hydroxyl and carbonyl groups. This permits the preparation of intermediate compounds, and in the preparation of Alizarin Bordeaux B for instance the reaction can be stopped at the stage of Brilliant Alizarin Bordeaux R. (2) The oxidizing action of concentrated sulfuric acid may be utilized at 160–200°, the presence of a trace of selenium as a catalyst being essential. At such high temperatures decomposition can occur, and this is prevented by adding boric acid which imparts increased stability. (3) Oxidizing agents, e.g. sodium nitrite, may be added, together with a trace of mercury as catalyst. Using manganese dioxide and sulfuric acid, the product is an anthradiquinone, converted into the corresponding hydroxy compound by mild reduction. (4) By the action of fuming sulfuric acid and sulfur on 1,5-dinitroanthraquinone, or a mixture of the 1,5- and 1,8-compounds, a complex series of reactions occur (cf. the formation of Naphthazarin



Quinalizarin

Alizarin Cyanine NS

from the dinitronaphthalenes). Through the intermediate stages of anthraquinone-1,4,5,8-diquinonimine and anthratriquinone, 1,4,5,8-tetrahydroxyanthraquinone is formed, and by the further action of sulfur trioxide and sulfuric acid, the product is 1,2,4,5,6,8-hexahydroxyanthraquinone-3,7-disulfonic acid (Anthracene Blue SWX) (Bohn, 1891; CI 1063). Hydrolysis by means of sulfuric acid finally yields the hexahydroxyanthraquinone, Anthracene Blue WR (B) (Alizarin Cyanine R, By) (Bohn, 1891; CI 1062).



Anthracene Blue SWX

Anthracene Blue WR

When an anthraquinone-β-sulfonic acid substituted by a hydroxyl group in the adjacent α-position is fused with alkali, replacement by a hydroxyl group takes place normally as in the benzene and naphthalene series. Thus 1,2,5,6-tetrahydroxyanthraquinone is obtained in good yield by heating anthrarufin-2,6-disulfonic acid with caustic soda and sodium chlorate at 260–270°.[29]

Alizarin Bordeaux B dyes bordeaux-red on aluminum and dark violet-blue on chromium. The dye gives sensitive color reactions with various metallic ions, e.g., Be, Zr, Th;[30] and it has been used for the estimation of minute amounts of boron in steel. The shades from Alizarin Cyanine NS (By; CI 1050) are red-violet on aluminum and reddish blue on chromium; the latter has good fastness and is more useful. Wool is dyed a fast blue from a single bath containing chromium salts. Anthracene Blue WR dyes violet on aluminum and blue on chromium, and it is an important dye for dyeing wool in all forms and for dyeing leather. Alizarin Cyanine Black G (3-nitro-1,2,4,5,7,8-hexahydroxyanthraquinone) (By; CI 1065), prepared by heating 3-nitroanthrapurpurin with manganese dioxide and oleum, gives a fast black on wool by afterchroming.[31]

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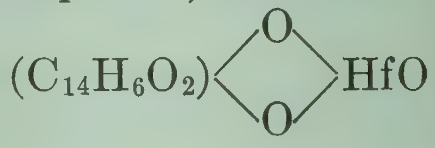
[29] Marshall, *JCS* 254 (**1937**).

[30] Komarowsky and Korenmann, *Z. anal. Chem.* **94**, 247 (1933).

PROPERTIES AND REACTIONS OF THE HYDROXYANTHRAQUINONES

The hydroxyanthraquinones vary in color from yellow to red. The absorption spectra in neutral and alkaline solution are characteristic and can be used for identifying the compounds.[32] The colorations in sulfuric acid, and the color changes produced by adding boric acid to the sulfuric acid solution, are valuable reactions for characterizing the hydroxyanthraquinones, and these colorations may be studied visually or spectroscopically.[32] Alizarin and many of the other hydroxyanthraquinones, as well as their sulfonic acids, undergo color changes with change in pH, and they have therefore been occasionally used as indicators. Alizarin in alcoholic solution changes in color from yellow to violet at pH 5.5–6.8.

The hydroxyanthraquinones are useful as colorimetric reagents for the detection and estimation of metals,[33] e.g., Zr and Hf in small amounts may be determined.[34] Spectrophotometric evidence has been obtained to show that the hafnium-alizarin lake is a definite compound, not a coordination complex like the aluminum lake, but a salt  $(C_{14}H_6O_2)\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle HfO$ in which both the hydroxyl groups are involved.

The α-hydroxyl group exhibits characteristic properties indicating chelation with the neighboring carbonyl group. α-Hydroxyanthraquinones form crystalline compounds with boracetic anhydride,[35] and the lake-forming properties of the mordant dyes of the anthraquinone series are primarily dependent on the presence of one or more α-hydroxyl groups, although the presence of a second hydroxyl group ortho to an α-hydroxyl is necessary for useful mordant-dyeing properties. α-Hydroxyl groups are much more resistant to methylation than β-hydroxyls, and Alizarin for instance yields the 2-monomethyl ether under ordinary conditions of methylation. Like anthraquinone and its other derivatives, the hydroxyanthraquinones may be reduced to the leuco compounds or anthrahydroquinones by means of hydrosulfite and alkali, and to anthrones or anthranols by acid reduction. Perkin[36] has made an extensive study of the reduction products of the hydroxyanthraquinones, and has shown that the presence of an α-hydroxyl group retards reduction, but if hydroxyl groups are also present in the β-position, ready reduction takes place; thus Alizarin undergoes reduction to deoxyalizarin (I), the corresponding anthranol in which the carbonyl adjacent to a hydroxyl group undergoes reduction. β-Hydroxyanthraquinone with zinc and ammonia gives 3,3′-dihydroxydianthrone (II), 3-hydroxyanthranol, and 2,2′-dihydroxydianthryl. The action of zinc dust and 20% caustic soda solution on β-hydroxyanthraquinone in an autoclave gives 2-hydroxy-9,10-dihydroanthracene.[37] The removal of a hydroxyl group by reduction is another characteristic reaction in the anthraquinone series. If sodium anthraquinone-β-sulfonate is fused with alkali in the absence of an oxidizing agent, some anthraquinone is formed by such reduction. Purpuroxanthin or xanthopurpurin (1,3-dihydroxyanthraquinone) can be conveniently prepared from Purpurin by reduction with zinc dust and ammonia.[38] On exposure to air in caustic soda solution, Purpuroxanthin gives Purpurin.

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[31] Schmidt, *J. Soc. Chem. Ind.* **33,** 1040 (1914).

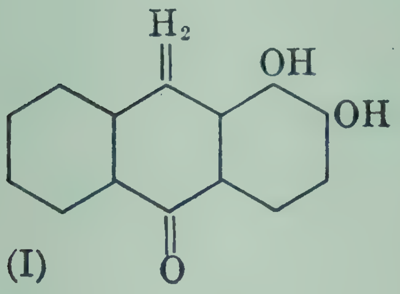
[32] Meek and Watson, *JCS* **109,** 544 (1916).

[33] See Fiegl, Qualitative Analyse mit hilfe von Tupfelreaktionen, Akademische Verlagsgesellschaft, Leipzig, 1938.

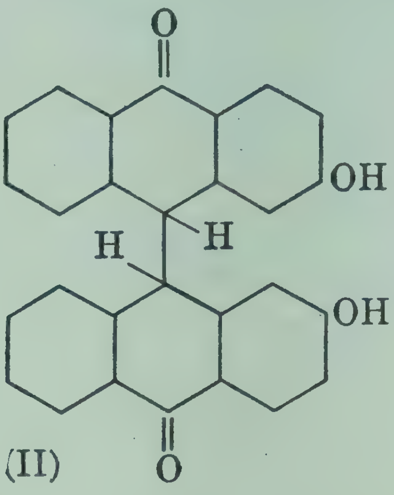
[34] Liebhafsky and Winslow, *JACS* **60,** 1776 (1938); **69,** 1130 (1947).

[35] Dimroth and Faust, *Ber.* **54,** 3020 (1921).

[36] Perkin and Haddock, *JCS* 541 (**1938**), and earlier papers.

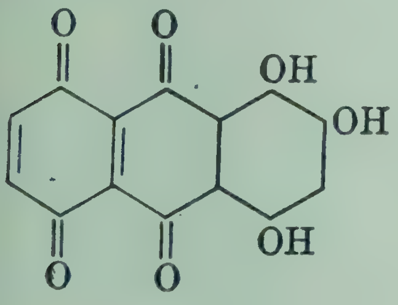


(I)

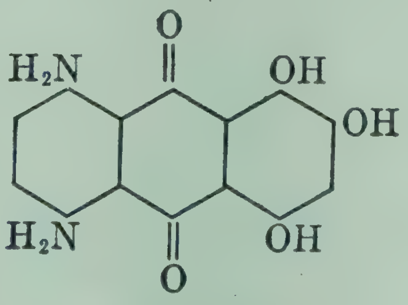


(II)

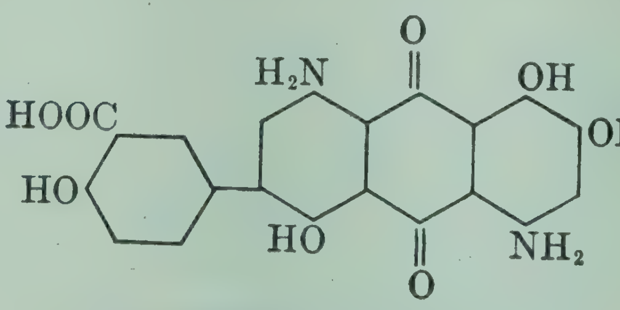
Quinizarin is readily oxidized to 1,4,9,10-anthradiquinone, e.g., by means of manganese dioxide and sulfuric acid, and Quinizarin can be regenerated by reduction of the diquinone with sulfur dioxide. Alizarin Cyanine RR, Alizarin Cyanine G and Alizarin Brilliant Cyanine GG, prepared from Quinalizarin, illustrate some of the technically important reactions which polyhydroxyanthraquinones containing 1,4-hydroxyl groups, like Quinizarin itself, can undergo.[25] Alizarin Cyanine RR (IG)



(III)



Alizarin Cyanine G



Alizarin Brilliant Cyanine GG

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[37] Braun and Bayer, *Ann.* **472**, 105 (1929).

[38] MLB, DRP 212,697.

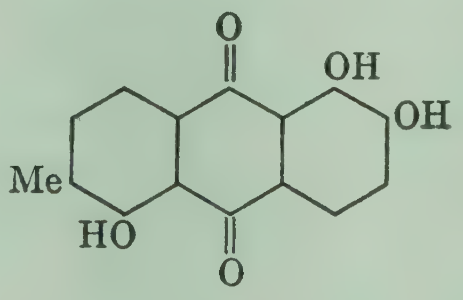
(1-amino-2,5,8-trihydroxyanthraquinone) is prepared by heating Quinalizarin (2.54 parts) with water (30), 50% caustic soda solution (20), 40% sodium bisulfite (0.2) and 100% ammonia (0.9) at 70° in an autoclave for 10 hours.[5] For the other two dyes, Quinalizarin is first oxidized to the diquinone (III) by manganese dioxide and sulfuric acid. Condensation of (III) with ammonia gives Alizarin Cyanine G (CI 1051). Condensation of (III) with salicylic acid and treatment of the product with ammonia gives Alizarin Brilliant Cyanine GG.[39] These dyes yield bluish green shades on chrome-mordanted wool, but have now been replaced by their analogs containing sulfonic groups which have better dyeing properties.[25] Such aminohydroxyanthraquinones and their derivatives are, however, useful as cellulose acetate dyes.

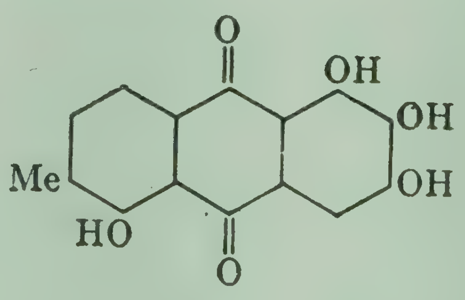
Natural Anthraquinone Coloring Matters[40]

Anthraquinone derivatives are widespread in nature, and have been isolated from roots, lichens, fungi and insects; the occurrence of a polyhydroxyanthraquinone in the mineral kingdom has also been reported.[40] The natural coloring matters of the hydroxyanthraquinone type are often accompanied by *C*-methyl derivatives and by hydroxymethylanthranols, which are usually nontinctorial constituents.

Madder contains besides alizarin a series of anthraquinone derivatives: purpurin, its 3-carboxylic acid (pseudopurpurin), xanthopurpurin and its 2-carboxylic acid (munjistin), and rubiadin (1,3-dihydroxy-2-methylanthraquinone). Chay root (*Oldenlandia umbellata*) contains alizarin, its α-methyl ether, anthragallol methyl ethers, and hystazarin monomethyl ether (2-hydroxy-3-methoxyanthraquinone). The roots of *Morinda citrifolia*, used in India at one time for dyeing reds, purples and chocolates on suitable mordants, contain a glycoside of morindone, 1,2,5-trihydroxy-6-methylanthraquinone. The isomeric chrysarone, 3,5,6-trihydroxy-2-methylanthraquinone, occurs in the root of *Rheum rhaponticum*. From the Australian shrub, *Coprosma areolata*, two anthraquinone derivatives, rubiadin-1-methyl ether and areolatin, have been isolated in the phenomenally high yield of 23%. The constitution

Morindone





Areolatin

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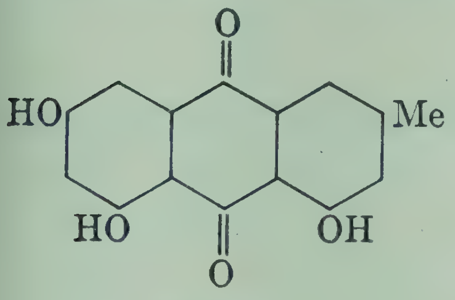
[39] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935.

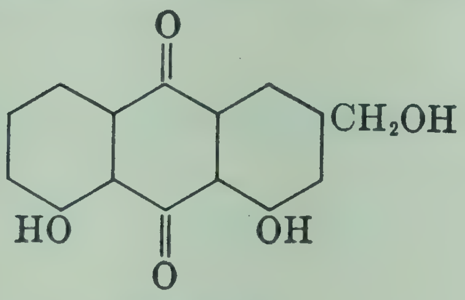
[40] Ref. 1, Chapter XXIV (see p. 740). See also Eder and Siegfried, *Pharm. Acta Helv.* **14**, 34 (1939).

of areolatin has been confirmed synthetically by the condensation of 2-hydroxy-*p*-toluic acid with gallic acid in presence of sulfuric acid.[41] The bark of *Coprosma lucida* contains a large quantity of anthraquinone compounds present in the free state or as glycosides, and as many as eight of the nonglycosidic compounds have been isolated by chromatographic adsorption on calcined magnesia;[41] these are anthragallol, its 2-methyl and 1,2-dimethyl ethers, 1,6-dihydroxy-2-methylanthraquinone, rubiadin, 3-hydroxy-2-methylanthraquinone, a new anthraquinone coloring matter (lucidin, probably 1,3,5-trihydroxy-2-methylanthraquinone), and a minute amount of an unidentified compound. Several of these anthraquinones occur in *Coprosma acerosa*, which contains for instance 1,6-dihydroxy-2-methylanthraquinone, probably identical with a constituent of *Morinda umbellata* and with soranjidiol from *Morinda citrifolia*.[41] Teloschistin, isolated from an Indian lichen, is 1,8-dihydroxy-3-methoxy-6-hydroxymethylanthraquinone.[41a]

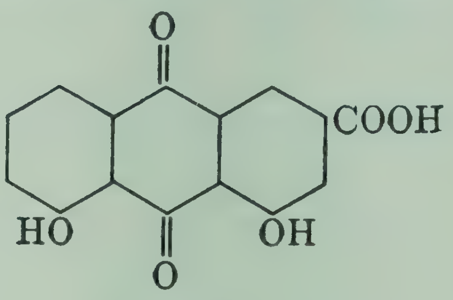
Anthraquinone derivatives in the free state or as glycosides are present in many cathartic drugs, such as rhubarb, senna, cascara and aloes. Examples are chrysophanic acid, emodin and aloe-emodin, and rhein.



Emodin

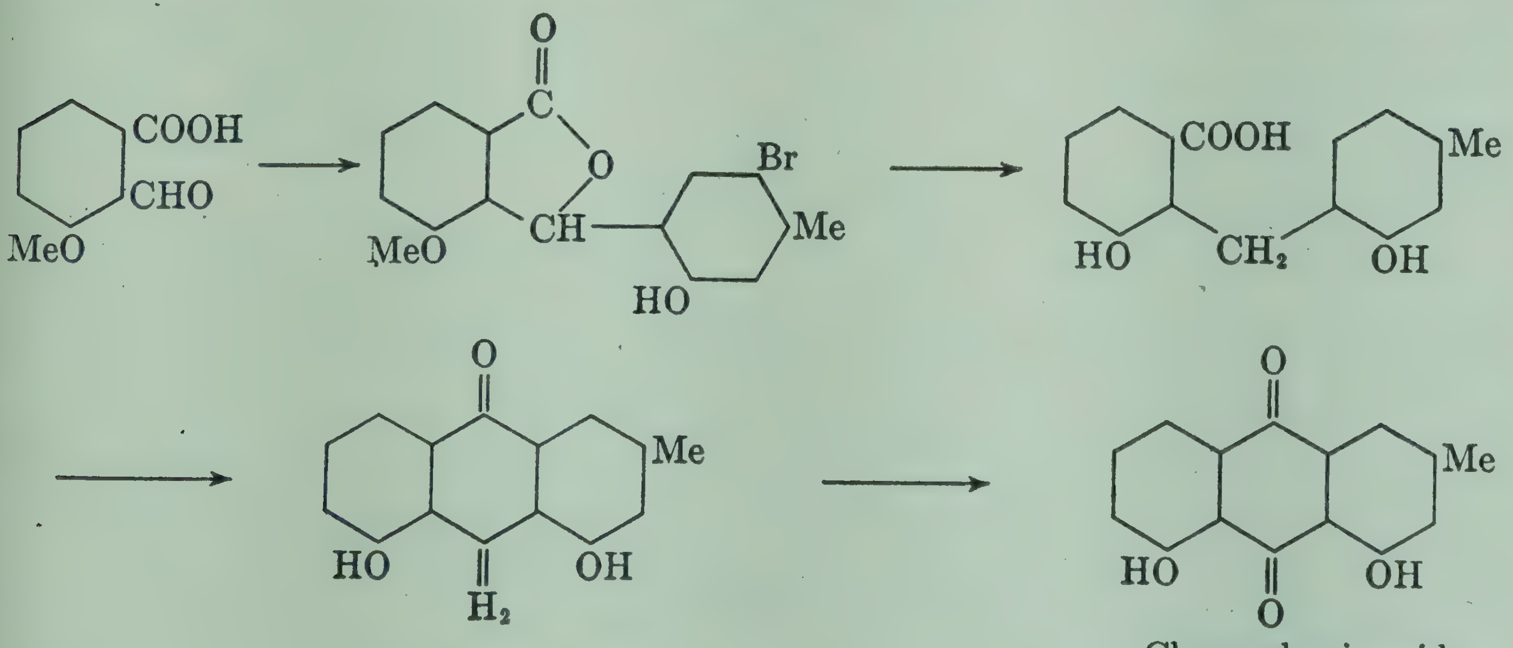


Aloe-emodin



Rhein

Anthrones and anthranols have also been isolated from some of the purgative drugs. Chrysophanic acid has been synthesized by the indicated route which confirms its constitution (Naylor and Gardner).[40]



Chrysophanic acid

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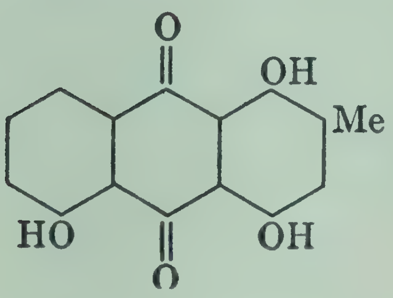
[41] Briggs *et al.*, *JCS* 568, 990 (**1948**); *ibid.* 1241, 1246 (**1949**).

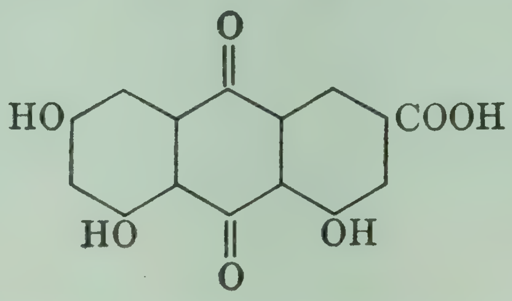
[41a] Seshadri and Subramanian, *Proc. Indian Acad. Sci.* **30A**, 67 (1949).

An earlier synthesis of Eder and Widmer[42] involves an interesting reaction which is applicable to the synthesis of other 1,8-dihydroxyanthraquinone derivatives. When 3-nitrophthalic anhydride was condensed with *m*-cresol in large excess in presence of aluminum chloride, a 90% yield of 2-(2′-hydroxy-4′-methyl)benzoyl-3-nitrobenzoic acid was obtained; cyclization and replacement of the nitro group by hydroxyl gave chrysophanic acid. Emodin was synthesized similarly from 3,5-dinitrophthalic anhydride.[42]

Raistrick[40] has isolated several hydroxyanthraquinones from the metabolic products of fungi. Examples are helminthosporin (4,5,8-trihydroxy-2-methylanthraquinone), catenarin (1,4,5,7-tetrahydroxy-2-methylanthraquinone), cynodontin (1,4,5,8-tetrahydroxy-2-methylanthraquinone), and tritisporin (1,3,5,8-tetrahydroxy-6- or 7-hydroxymethylanthraquinone)[43] from various species of *Helminthosporium;* emodic acid and ω-hydroxyemodin from *Penicillium cyclopium* Westling; and islandicin (1,4,5-trihydroxy-2-methylanthraquinone) from *Penicillium islandicum* Sopp.[44] The constitution assigned by Howard and Raistrick to islandicin has been confirmed by unambiguous synthesis.[45] 2-(5′-Benzeneazo-2′-hydroxy-4′-methyl)-benzoyl-3-nitrobenzoic acid, obtained by coupling 2-(2′-hydroxy-4′-methyl)-benzoyl-3-nitrobenzoic acid with diazotized aniline, gave on reduction 3-amino-2-(5′-amino-2′-hydroxy-4′-methyl)-benzoylbenzoic acid; tetrazotization and treatment with 96% sulfuric acid at 150° simultaneously effected hydrolysis of the diazonium groups and cyclization to the desired anthraquinone. Boletol, the red coloring matter of the stalks of various species of the fungus *Boletus*, is purpurin-5- or 8-carboxylic acid.[40]



Islandicin



Emodic acid

Cochineal, kermes, and lac dye, prepared from the dried bodies of certain insects or their exudates, have been known and used as coloring materials from ancient times. They have not survived in competition with the coal-tar dyes for dyeing textiles, but still find limited use for other purposes, particularly cochineal for coloring cosmetics and foods. Carminic acid, kermesic acid, and laccaic acid, the essential coloring matters of cochineal, kermes, and lac dye are closely allied in their properties and constitution; our knowledge of their chemistry is mainly due to Dimroth. The evidence in favor of the proposed structures for carminic and kermesic acids is extensive, but not conclusive, regarding especially the side chains. The constitution of laccaic acid is much more ambiguous.[40]

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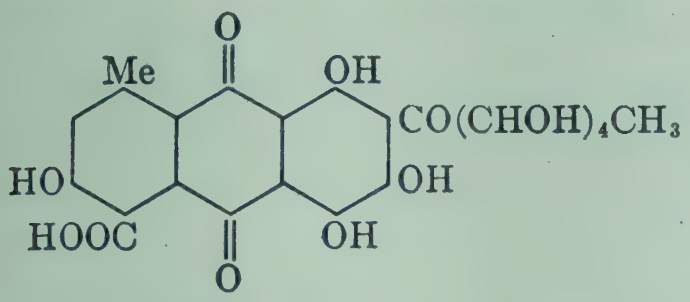
[42] Eder and Widmer, *Helv. Chim. Acta* **5,** 3 (1922); **6,** 419, 966 (1923); Eder and Hauser, *ibid.* **8,** 126 (1925); Eder, DRP 397,316. For a detailed study of the condensation of 3- and 4-nitrophthalic anhydride with phenols and phenolic ethers, see Mitter and Dutt, *J. Indian Chem. Soc.* **13,** 228 (1936).

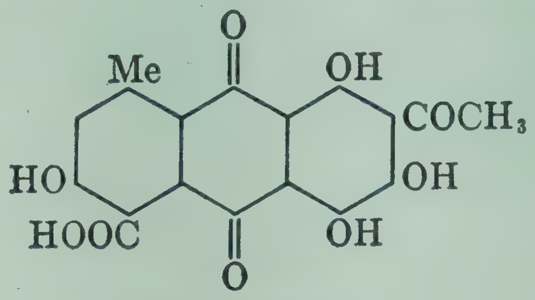
[43] Raistrick, Robinson, Charles and ICI, BP 420,362; see for synthesis, Marriott and Robinson, *JCS* 1631 (**1934**).

[44] Howard and Raistrick, *Biochem. J.* **44,** 227 (1949).

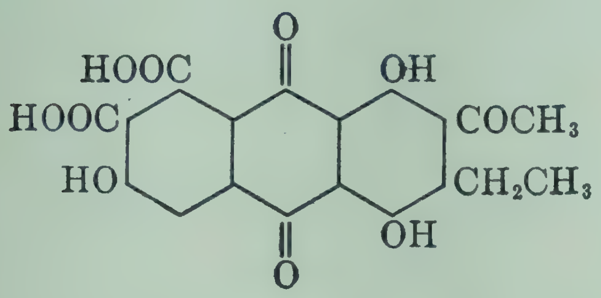
[45] Joshi, Tilak and Venkataraman, *Proc. Indian Acad. Sci.* **32A,** 348 (1950).



Carminic acid



Kermesic acid



Laccaic acid

CHAPTER XXIX

ACID ANTHRAQUINONE DYES

Graebe and Liebermann (1871) observed that Alizarin could be made applicable to wool as an acid-mordant color by the simple process of sulfonation. The 3-sulfonic acid, Alizarin Red S, dyed wool in scarlet shades in conjunction with aluminum, and bordeaux with chromium. Laubmann's discovery in 1893 that faster and more brilliant acid and acid-mordant dyes of the anthraquinone series could be produced by the introduction of amino and sulfonic groups was of great importance, since some of the most valuable and widely used dyes for wool and silk belong to this type; Acid Alizarin Blue GR (MLB) (4,8-diamino-1,3,5,7-tetrahydroxyanthraquinone-2,6-disulfonic acid), dyeing blue with chromium, was the first commercial representative. Alizarin Cyanine Green (By) was made by Schmidt a year later from Quinizarin, an intermediate from which several other fast and brilliant acid colors have since been prepared. The predominant shades in the series of anthraquinone acid dyes are blues and greens, which are characterized by their excellent fastness to light. With the exception of the azo dyes, the anthraquinone sulfonic acids constitute the most important group of dyes for wool and silk, and the continued interest in the field may be judged by the intense patent activity. One advantage of the acid anthraquinone dyes is that they leave cellulose fibers unaffected and are therefore useful for cross-dyeing union materials of the cellulose fibers and wool or silk.

The anthraquinone acid dyes[1, 2, 3] may be classified into five groups: (1) sulfonic acids of the hydroxyanthraquinones; (2) sulfonic acids of amino- and arylaminoanthraquinones; (3) dyes containing both hydroxyl and amino or arylamino groups; (4) pyridanthrone, pyrimidanthrone and other heterocyclic derivatives; and (5) cellulose acetate type of dyes.

HYDROXYANTHRAQUINONESULFONIC ACIDS

Unlike phenols and naphthols in which the hydroxyl groups greatly facilitate sulfonation, the hydroxyanthraquinones require as severe conditions for sulfonation as anthraquinone itself; but the hydroxyl

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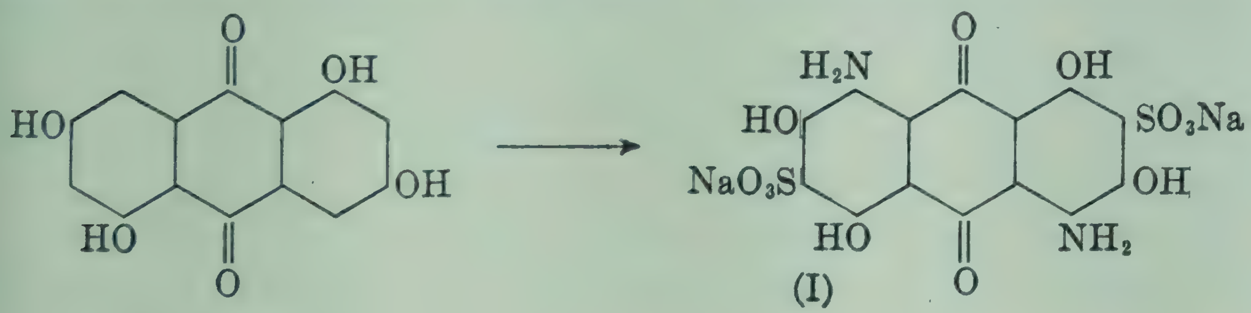
[1] Richter in Thorpe's Dictionary of Applied Chemistry, Vol. I, Longmans, London, 1937, p. 229.

[2] Thomson, *ibid.*, p. 404.

[3] *BIOS* **1484.**

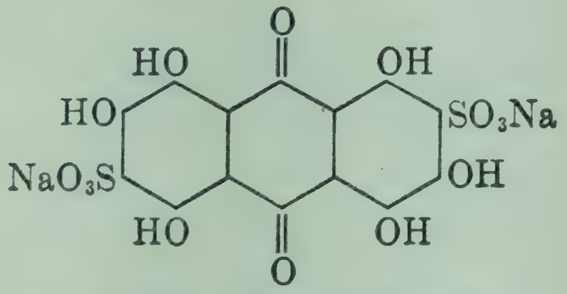
groups orient the sulfonic groups in adjacent β-positions. In presence of a mercury salt, β-sulfonation still takes place in the hydroxylated nucleus, but if one of the terminal rings is unsubstituted, mercury has the usual effect of inducing α-sulfonation. Thus the disulfonation of Alizarin gives the 3,6- and 3,7-disulfonic acids in the absence of mercury, and the 3,5- and 3,8-disulfonic acids in presence of mercury.

Alizarin Red S (Graebe and Liebermann, 1871; CI 1034), 2S (CI 1040) and 3S (CI 1044) are the 3-monosulfonic acids of Alizarin, Anthrapurpurin and Flavopurpurin.[4] On wool, they are much easier to apply than the parent mordant dyes; brighter shades are obtained, and the levelling and fastness properties are good. Alizarin Red S is a largely used dye, applicable to wool as an acid color; subsequent treatment with alum gives red shades and with dichromate or chromium fluoride bordeaux shades, which are fast to light and milling. Anthracene Blue SWX (Bohn, 1891) (BASF; CI 1063) (Acid Alizarin Blue BB), the disulfonic acid of Anthracene Blue WR, may be prepared by the same method of heating 1,5- and 1,8-dinitroanthraquinone with sulfur, fuming sulfuric acid and boric acid;[4] the disulfonic acid is the penultimate stage in the production of the hexahydroxyanthraquinone. An alternative method is to sulfonate, nitrate and reduce Anthrachrysone to (I), and replace the amino by hydroxyl groups by means of boiling caustic soda solution. Anthracene Blue SWX dyes wool a cherry red from an acid bath, changed to a fast, bright, pure blue by treatment with chromium fluoride. Alizarin Cyanine BBS is monosulfonated hexahydroxyanthraquinone.



Anthrachrysone

(I)



Anthracene Blue SWX

Sulfonic Acids of Amino and Arylaminoanthraquinones

A general reaction (Schmidt, 1894–1897), which is of value for the synthesis of dyes of this group as well as the next, is to heat a di- or polyhydroxyanthraquinone with ammonia or primary aromatic amines. If there are hydroxyl groups present in both α- and β-positions, the α-hydroxyls are preferentially replaced, and usually those in the same benzene ring. This, however, is not an invariable rule, and in Purpurin for instance the β-hydroxyl and one of the α-hydroxyls are replaced by heating with aniline. By using the leuco derivative of the hydroxyanthraquinone for the condensation the reaction proceeds more smoothly and in better yield; the product is the leuco derivative of the desired amine, and the aminoanthraquinone is finally isolated by oxidation. Whether a hydroxyanthraquinone or its leuco derivative is used for the condensation, boric acid is a useful catalyst. The hydroxyanthraquinones which are of primary interest for this reaction are Quinizarin and its derivatives; and one or both of the hydroxyl groups in Quinizarin may be replaced by amino, alkylamino or arylamino groups by using suitable conditions for the condensation.

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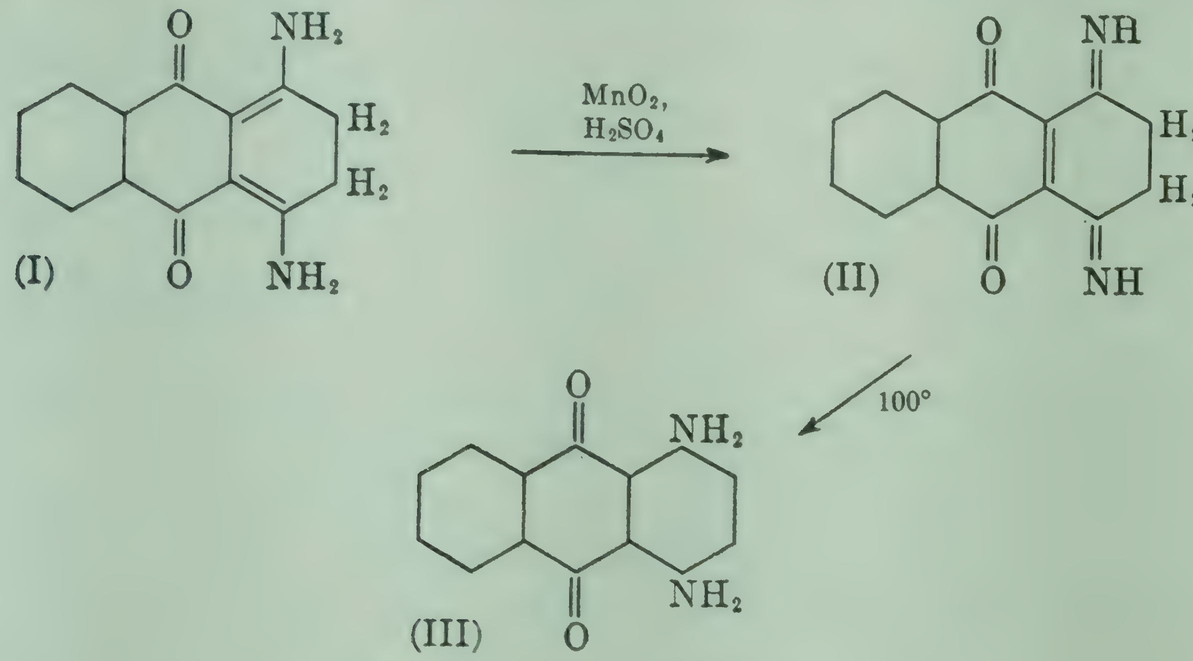
[4] See Chapter XXVIII.

When leucoquinizarin is heated with ammonia, 1,4-diamino-2,3-dihydroanthraquinone (I) is formed; oxidation by manganese dioxide and sulfuric acid gives the diimide (II), which isomerizes to 1,4-diaminoanthraquinone (III) on heating at about 100°. Leuco-1,4-diaminoanthraquinone can be oxidized to (III) by heating at 150° a solution in nitrobenzene to which a little piperidine is added.[5] Sulfonation of leuco-1,4-diaminoanthraquinone in presence of boric acid gives Alizarin Direct Violet EBB; purification through the calcium salt yields the EFF brand, also called Anthralan Violet 6B (IG).[6] The trisulfonic acid of (III), prepared by monosulfonating 2,3-dichloro-1,4-diaminoanthraquinone and then treating with sodium sulfite, dyes wool clear



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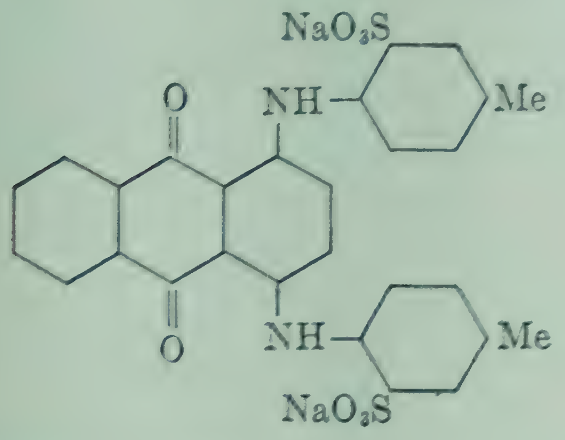
[5] *BIOS* **1493**.

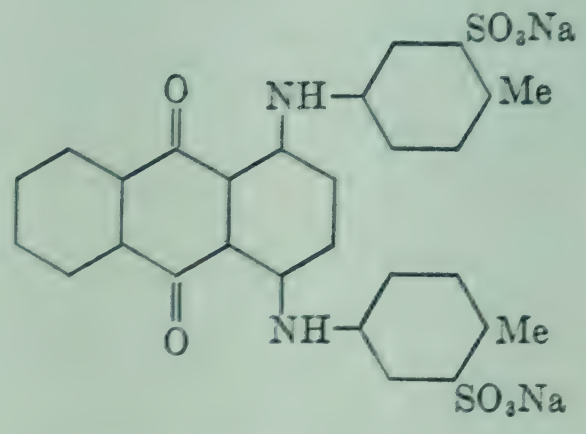
[6] Report 19, Textile Series, Office of the Quartermaster General, U.S. Dept. of Commerce.

blue shades of excellent fastness.[7] Alizarin Irisol RL is the monosulfonic acid of 2,3-dichloro-1,4-diaminoanthraquinone.[8]

When leucoquinizarin is condensed with two moles of *p*-toluidine, the vat oxidized, and the di-*p*-toluidinoanthraquinone sulfonated, the product is the important dye, Alizarin Cyanine Green G (Schmidt, 1894; Solway Green G, ICI).[8, 9] Dyed from an acid bath, the shades on wool are yellowish to bluish green, and the fastness to milling is increased by afterchroming. Using *p*-aminodiphenyl in place of *p*-toluidine for the quinizarin condensation, and sulfonating the product Alizarin Cyanine Green GT is obtained; using 1,2,3,4-tetrahydro-2-naphthylamine, the product is Alizarin Supra Blue SE.[3] Blue to green dyes with excellent fastness properties are obtained by condensing 6-chloro- or 6,7-dichloroquinizarin with two moles of various amines (e.g. aminomesitylene; 1,3-diphenyl-2-aminopropane) and sulfonating the product.[10] Fast blue to violet dyes, otherwise difficult to prepare, are obtained by heating leucoquinizarin with sodium 1,2-diphenylethylaminemonosulfonate and other aminesulfonates.[10a]



Alizarin Cyanine Green G



Alizarin Direct Green G

Alizarin Cyanine Green cannot be prepared by direct condensation of leucoquinizarin and *p*-toluidine-3-sulfonic acid; but the isomeric toluidinesulfonic acid in which the sulfonic group is *meta* to the amino group condenses, and the isomer was marketed by MLB as Alizarin Direct Green G (CI 1079).

Alizarin Cyanine Green can also be prepared from 1,4-dichloro- or dibromoanthraquinone by replacement of the halogen atoms by *p*-toluidino groups, and subsequent sulfonation; but this method is much more useful for dyes derived from 2,4-dibromo-1-aminoanthraquinone (IV), which is a valuable intermediate. The bromination of α-aminoanthraquinone to (IV) may be carried out in glacial acetic acid at 50° or nitrobenzene[11] at 150–160°; or by adding bromine (1.59 parts), and subsequently chlorine (0.65), to a suspension of α-aminoanthraquinone prepared by adding a solution in 10% oleum to water at 25°; the bromination is completed by heating at 70–80° for 3 hours (yield 97%).[8] When (IV) is heated with six times its weight of *p*-toluidine and a molar proportion of sodium acetate for 5 hours at 190°, cooled and diluted with methanol a nearly quantitative yield of (V) is obtained. Sulfonation of (V) with 5% oleum at 15–20° gives the important dye, Alizarin Sky Blue B (By) (Unger, 1899; CI 1088) (Alizarin Pure Blue B) (Solway Sky Blue BS; ICI).

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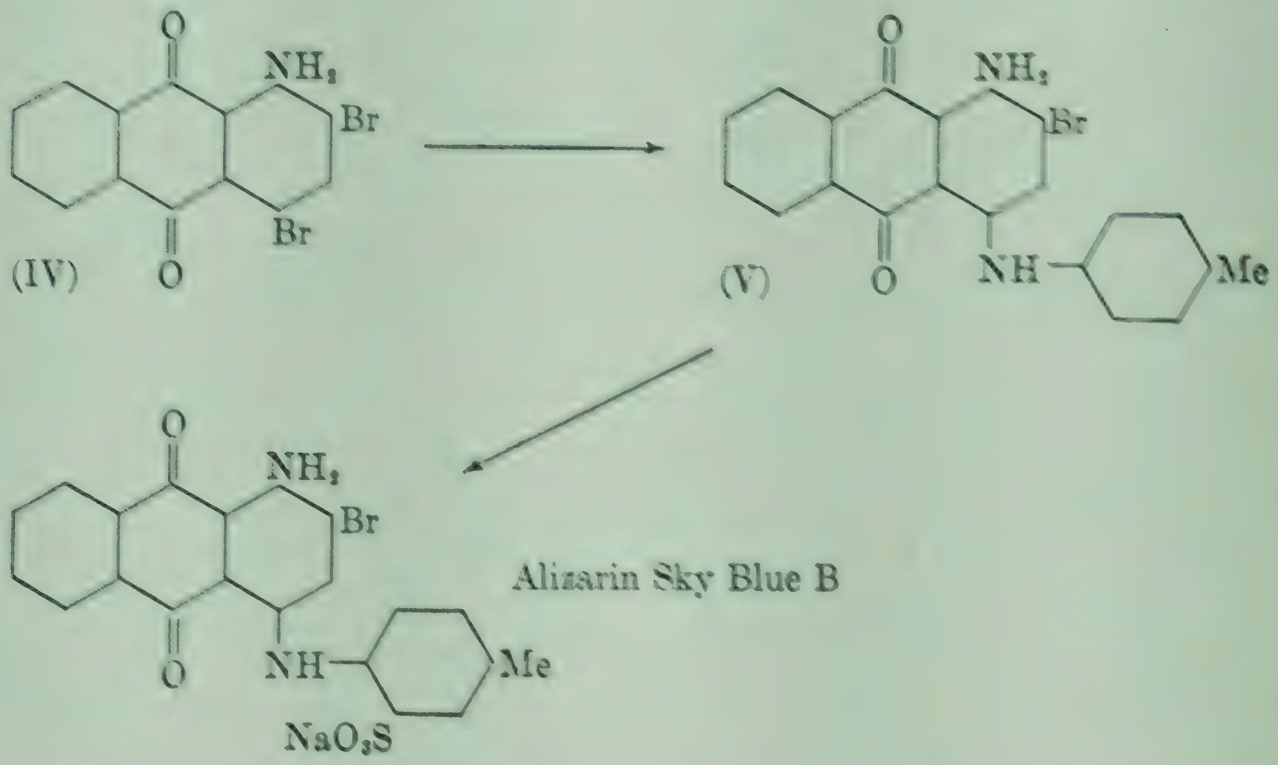
[7] IG, BP 419,954.

[8] *FIAT* **1313** II.

[9] Smith and Reid, *Chemistry and Industry* 675 (**1948**).

[10] Sandoz, SP 215,662; 247,987; BP 585,730; 597,478; USP 2,448,094; 2,494,240.

[10a] Tatum and ICI, USP 2,475,530.



By replacing the two bromine atoms in (IV) successively with suitable groups, useful acid dyes can be obtained; for example, blue, light-fast dyes for wool and nylon are obtained by condensing first with aniline, then replacing the 2-bromine by a thiol group, and reacting the latter with glycerol-α-monochlorohydrin.[12]

The condensation of 4-chloro-1-amino-2-methylanthraquinone with *p*-toluidine, followed by sulfonation, gives Cyananthrol R (BASF; CI 1076) (Alizarin Cyananthrol RXOF, IG)[8] (Solway Blue R, ICI), which dyes reddish blue shades of good light fastness (5–6). Using *m*-aminobenzenesulfon-*N*-methylanilide in place of *p*-toluidine in this reaction, the product is Alizarin Direct Violet BL.[13] Alizarin Astrol B is prepared from 1-bromo-4-methylaminoanthraquinone, which is obtained by the bromination of 1-methylaminoanthraquinone in 96% sulfuric acid at 10°; the light fastness is only 4. Anthraquinone Violet (Bally, 1898) (BASF; CI 1080) was prepared by the sulfonation of 1,5-bis-*p*-toluidinoanthraquinone, which may be obtained by the action of *p*-toluidine on

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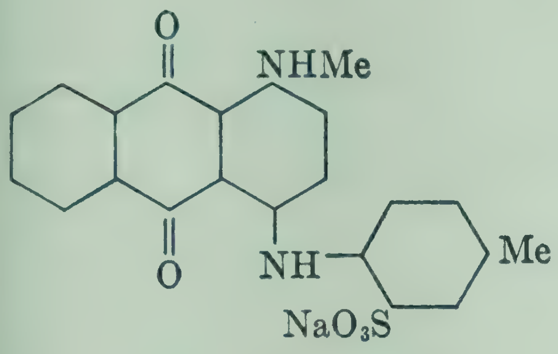
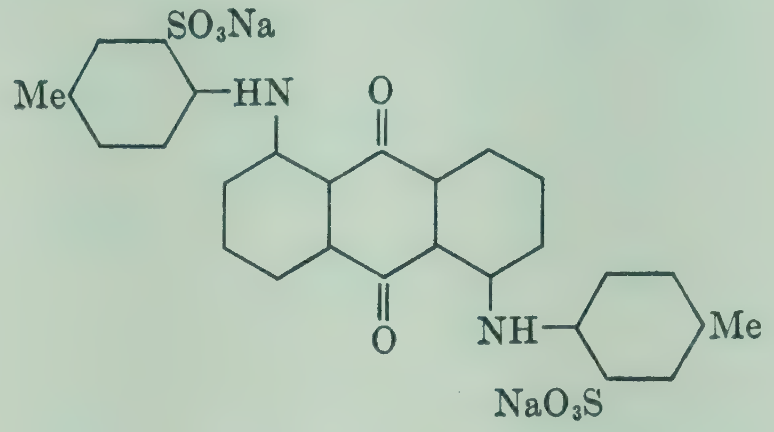
[11] Ullmann and Eiser, *Ber.* **49,** 2165 (1916).

[12] Grossmann and Ciba, USP 2,434,765.

[13] Microfilm FD 2537/46.

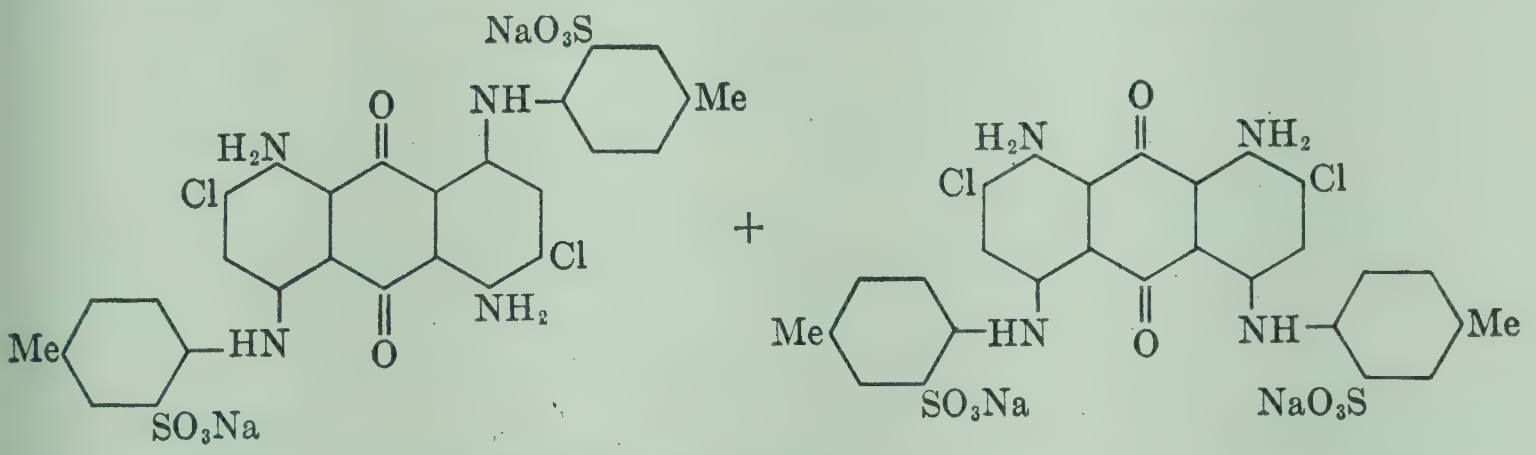


Alizarin Astrol B



Anthraquinone Violet

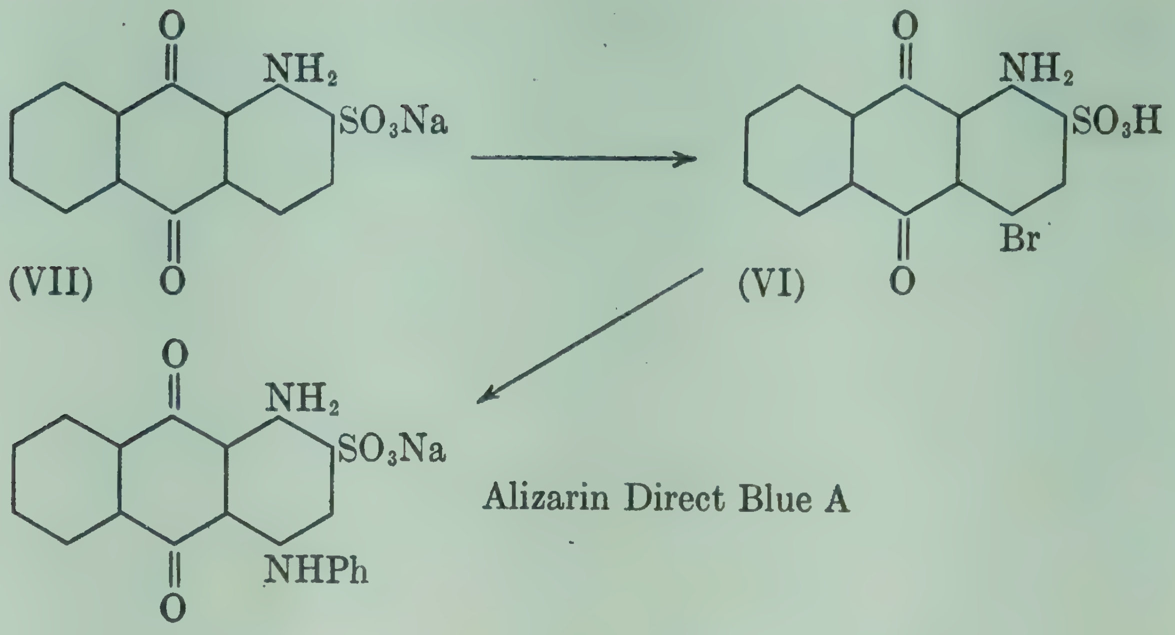
1,5-dichloro or 1,5-dinitroanthraquinone; but the IG brand is the sulfonation product of mixed 1,5- and 1,8-bis-*p*-toluidinoanthraquinone in a proportion of 7 to 11, the diamines being separately prepared from the dichloro compounds.[3] Anthraquinone Blue SRX (IG), which has light fastness 7, is prepared by the tetrachlorination of a mixture of 1,5- and



Anthraquinone Blue SRX

1,8-diaminoanthraquinone by means of sulfuryl chloride in *o*-dichlorobenzene, replacing the α-chlorine atoms by *p*-toluidine and sulfonating.[3] The bromine analog is Alizarin Pure Blue NA.[8]

1-Amino-4-arylaminoanthraquinone-2-sulfonic acids are very valuable and largely used wool colors, which dye bright, level shades with very good fastness to light and better washing fastness than the earlier acid anthraquinone dyes, although not of a milling color standard. These dyes are conveniently prepared from 4-bromo-1-aminoanthraquinone-2-sulfonic acid (VI), which is produced on a large scale for this purpose and for the preparation of anthraquinone vat dyes of the acridone type. By heating α-aminoanthraquinone (one part) with 20% oleum (11 parts) at 120° for 6 hours, diluting, salting out (VII), and proceeding with the bromination directly by adding bromine (0.8 part) and 16% hydrochloric

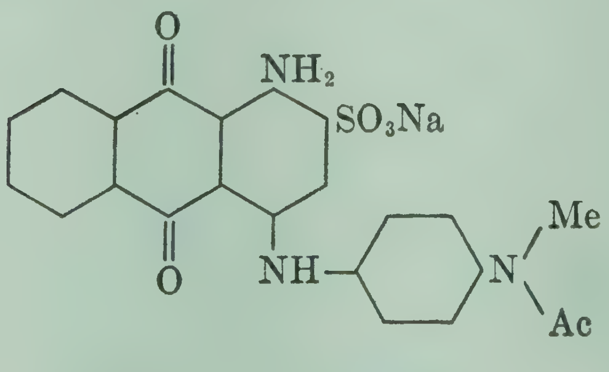


(VII) (VI)

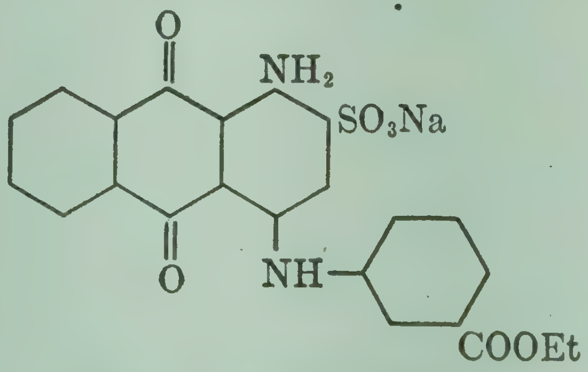
Alizarin Direct Blue A

acid (7 parts) at 0°, (VI) is produced in 70% yield;[14] (VII) can also be prepared by heating α-aminoanthraquinone with chlorosulfonic acid at about 130° *in vacuo*.[8] The bromo compound (VI) reacts readily with arylamines in boiling aqueous alkaline solution in presence of a copper salt. The aniline derivative is Alizarin Direct Blue A (MLB) (Herzberg, 1913) (Alizarin Saphirol A, IG)[3] (Solway Ultra Blue B, ICI),[2] the first arylaminoanthraquinone dye containing a sulfonic group in the anthraquinone part of the molecule. Dyes of this type can also be prepared from 2,4-dibromo-1-aminoanthraquinone (IV), via (V), which is heated with aqueous sodium sulfite under pressure.

Using cyclohexylamine in place of aniline for the condensation with (VI), the product is Alizarin Brilliant Pure Blue R (IG).[3] The same constitution has been assigned to Alizarin Saphirol A3R (IG) (Weinand, 1925),[15] but Alizarin Saphirol A3R or Anthralan Blue R is stated to have been prepared by condensing (VI) with *m*-aminobenzonitrile[13] or *p*-methylaminobenzonitrile.[8] The IG dyes, Alizarin Direct Blue AGG (Anthralan Blue G), Alizarin Direct Blue AR (Anthralan Blue B) and Alizarin Pure Blue FFB are similarly prepared respectively from *p*-aminoacetanilide, *p*-amino-*N*-methylacetanilide, and *m*-aminobenzoic acid; in the last case the carboxyl group is subsequently esterified.[16] These dyes



Alizarin Direct Blue AR



Alizarin Pure Blue FFB

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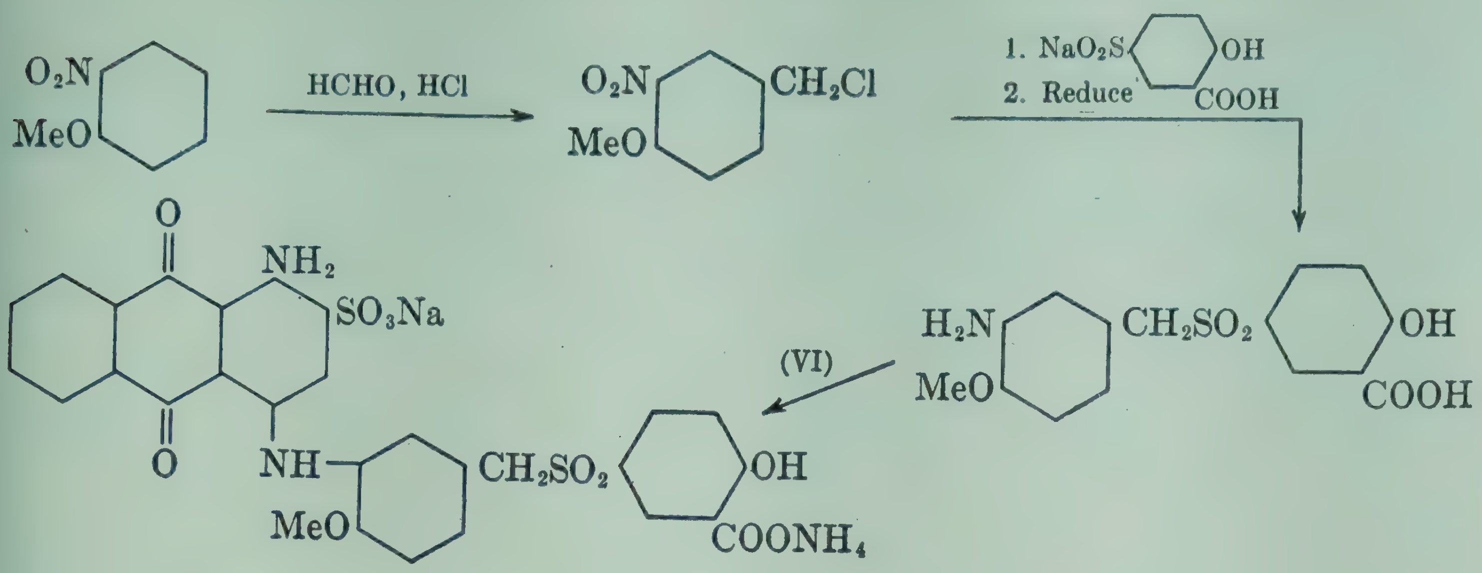
[14] Seymour *et al.*, USP 2,413,790; 2,440,760; British Celanese, BP 598,797.

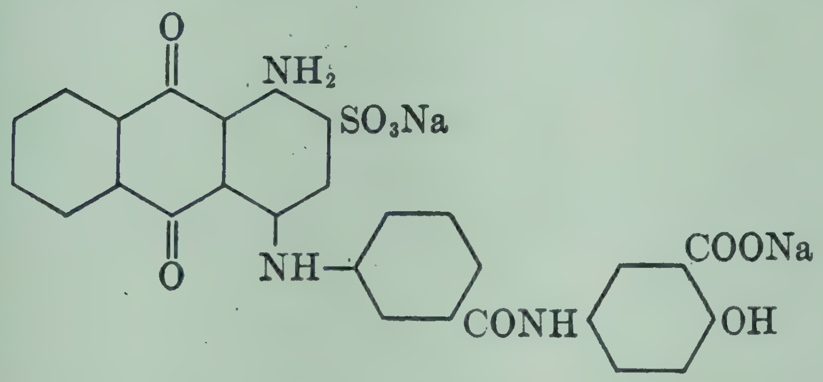
[15] Rowe, The Development of the Chemistry of Commercial Synthetic Dyes (1856–1938), Institute of Chemistry, London, 1938.

[16] *BIOS* **987**.


O₂N
MeO
HCHO, HCl
O₂N
CH₂Cl
MeO
1. NaO₂S
OH
2. Reduce
COOH
H₂N
CH₂SO₂
OH
MeO
COOH
(VI)
O
NH₂
SO₃Na
O
NH
CH₂SO₂
OH
MeO
COONH₄

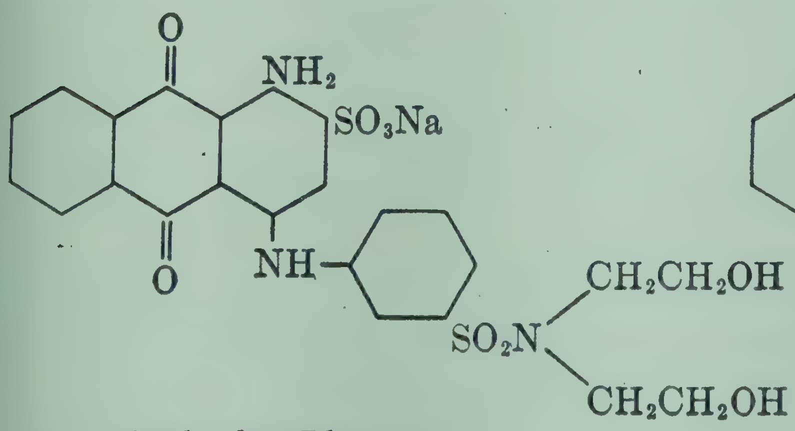
Alizarin Chrome Blue FFG

have excellent leveling power and light fastness (7), but their milling fastness is only 1–2. A more complex dye, which contains a salicylic acid residue so that it has mordant-dyeing properties, is Alizarin Chrome Blue FFG, prepared by the indicated series of reactions.[17] The analog starting from 4-nitro-*m*-xylene is Alizarin Chrome Blue FFR.[8] A similar dye, which IG was planning to market as a chrome mordant color for printing cotton, viscose and their unions, is Chrome Brilliant Blue BL, made by condensing (VI) with 5-(*m*-amino)benzamidosalicylic acid.[17, 18]

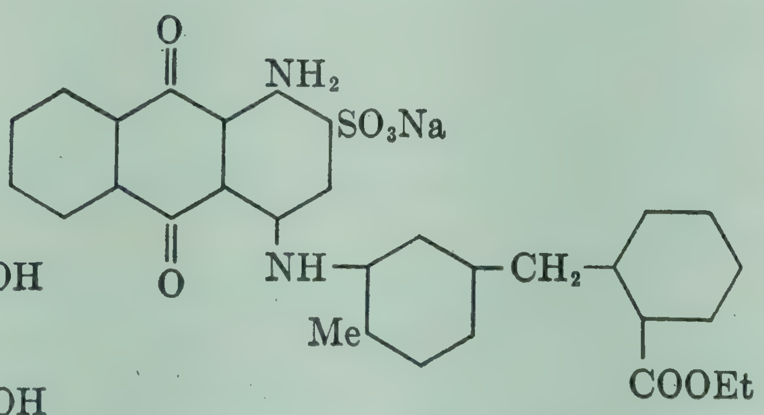

O
NH₂
SO₃Na
O
NH
COONa
CONH
OH

Chrome Brilliant Blue BL

For Anthralan Blue FR (IG), the amine condensed with (VI) is prepared from *m*-nitrobenzenesulfonyl chloride and diethanolamine.[6] Supranol Brilliant Blue G (IG), a fast and level-dyeing member of this group of dyes, is prepared from (VI) and 3-amino-4-methyldiphenylmethane-2′-carboxylic acid and subsequent esterification of the carboxyl group; the


O
NH₂
SO₃Na
O
NH
CH₂CH₂OH
SO₂N
CH₂CH₂OH

Anthralan Blue FR


O
NH₂
SO₃Na
O
NH
CH₂
Me
COOEt

Supranol Brilliant Blue G

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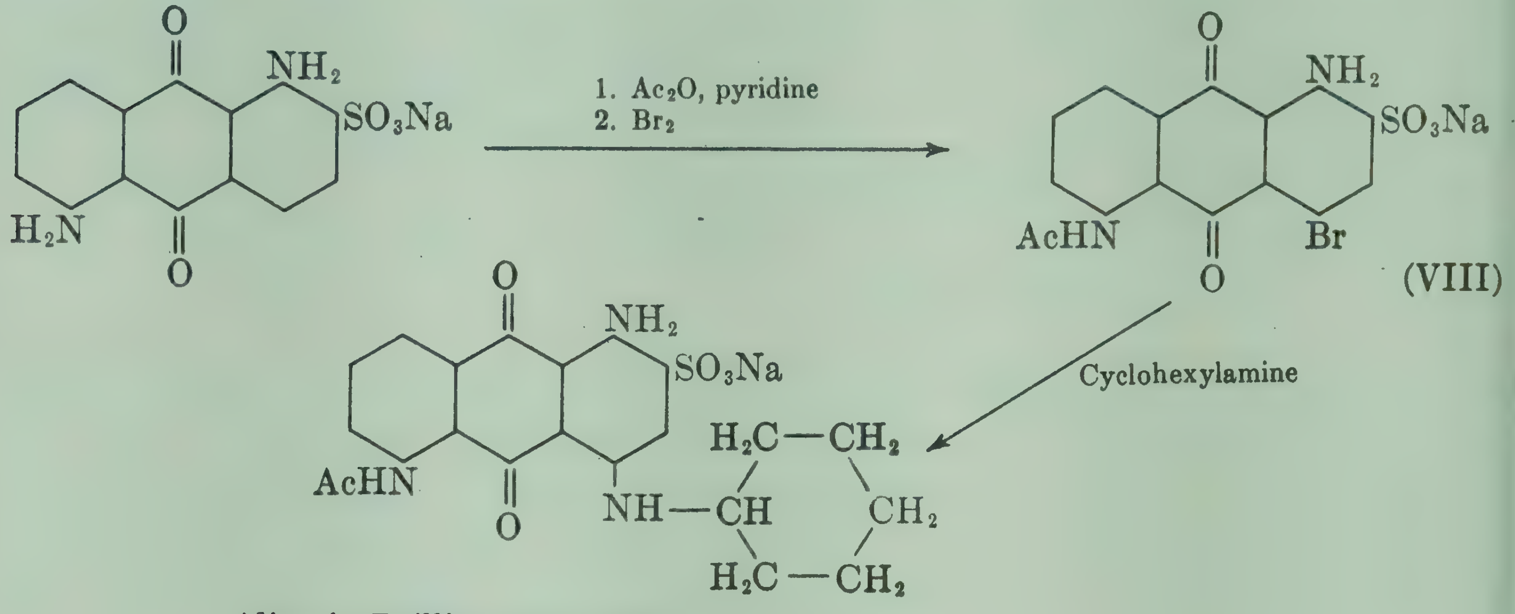
[17] *BIOS Misc.* **20.**

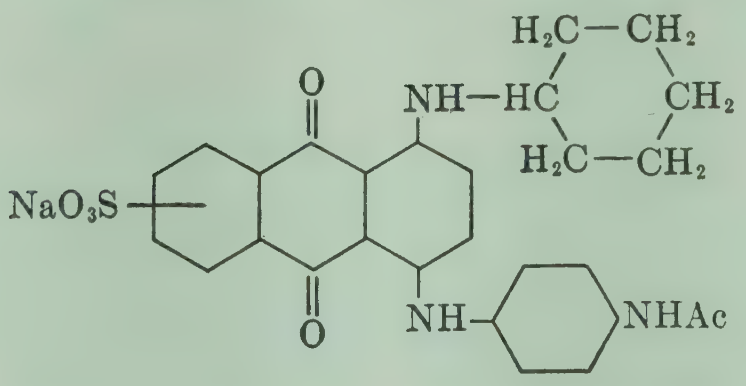
[18] IG, DRP 632,376.

required amine is prepared by the nitration and reduction of *p*-methylbenzoylbenzoic acid obtained by the condensation of toluene and phthalic anhydride.[6, 16] Alizarin Brilliant Pure Blue G (IG) is made from 1,5-diaminoanthraquinone-2-sulfonic acid, which is obtained in 54% yield by adding 1,5-diaminoanthraquinone (2 kg.) to 20% oleum (3.4 kg.) at 90°, heating at 145° for 3 hours, cooling to 125° and adding monohydrate (300 cc.), cooling to 100° and adding 78% sulfuric acid (3.5 kg.) in 2½ hours, and adding the charge to water (50 l.) and salt (3 kg.); the product is filtered, washed with salt solution, dissolved in ammoniacal water at 95°, filtered, and the filtrate acidified.[3, 18a] Replacing cyclohexylamine by *p*-aminoacetanilide for the condensation with (VIII), the product is Alizarin Direct Blue 6G (IG). A dye made from silver salt as starting material is Alizarin Brilliant Green B extra (IG). Silver salt is nitrated to a mixture of 1-nitroanthraquinone-6- and 7-sulfonic acids, which are condensed with cyclohexylamine, brominated (in aqueous pyridine) in the 4-position and finally condensed with *p*-aminoacetanilide.[3]



(VIII)

Alizarin Brilliant Pure Blue G

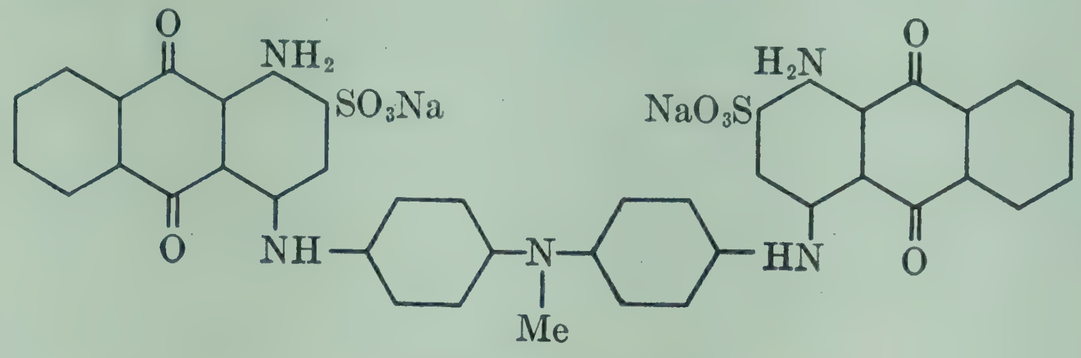


Alizarin Brilliant Green B extra

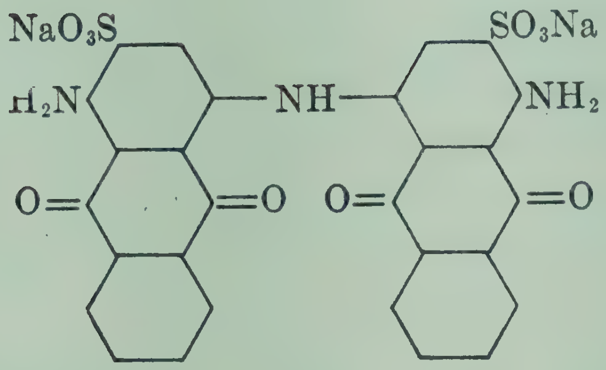
Two interesting symmetrically constituted dyes of this series are Supranol Blue GG and Alizarin Light (or Fast) Grey 2BL (By), 2BLW

[18a] According to *FIAT* **1313 II,** Alizarin Brilliant Pure Blue G has a similar constitution to that of Alizarin Direct Blue 6G, *p*-aminoacetanilide being replaced by *p*-toluidine.

(IG) (Raeder and Mieg, 1920); the latter is prepared by the sulfonation of 4,4′-diamino-1,1′-dianthrimide.[3] Alizarin Light Brown GL is sulfonated 1,1′-dianthrimide.[8]



Supranol Blue GG



Alizarin Light Grey 2BL

The solubility of Alizarin Sky Blue B and other acid anthraquinone dyes (e.g., Cyanine Green and Rubinol) can be increased by using the triethanolamine or the methylglucamine salts instead of the sodium salts.[19]

The importance of 4-bromo-1-aminoanthraquinone-2-sulfonic acid (VI) as an intermediate, and of the acid dyes derived from it by replacement of the bromine atom by arylamino groups is evidenced by the number of the patents in which the essential mode of preparation and the type of dye are retained, and modifications are suggested for increasing the brightness and fastness and for effecting minor alterations in the shades.[19a] Halogenation produces a hypsochromic effect, and the blue 1-amino-4-anilinoanthraquinone-2-sulfonic acid for instance gives a much redder dye on halogenation;[20] halogenation of dyes in which the anilino group carries alkyl and alkoxy substituents in the 2, 4, and 6-positions gives brilliant reddish blue shades.[21] Wool, silk, and nylon are dyed in fast level shades by dyes containing a trifluoromethyl group in the aryl residue.[22] Among the amines which have been condensed with (VI) are 3,5-dichloroanthranilic acid,[23] 3,4,5-trihalogenoanilines,[24] amides of aminobenzenecarboxylic acids, aminobenzonitriles, aminoacetophenones,[25] and arylaminesulfonamides in which the sulfonamide group is substituted by two hydroxyalkyl or one alkyl and one hydroxyalkyl groups.[26] The products from all these condensations are blue acid wool dyes.

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[19] Lee, Young, and du Pont, USP 2,314,356.

[19a] See also Bezzubets and Rozina, *J. Applied Chem. U.S.S.R.* **21**, 1152 (1948).

[20] IG, BP 480,270.

[21] Gutzwiller and Sandoz, USP 2,427,527. See also SP 242,846; 246,190–2.

[22] Wuertz, Lee, Buxbaum, and du Pont, USP 2,333,402.

[23] IG, BP 469,390.

[24] IG, BP 462,693.

Blue to reddish-blue dyes faster to soda boiling and washing than Alizarin Direct Blue AGG are obtained among the 1-amino-4-*p*-acylamidoanilinoanthraquinone-2-sulfonic acids when the alkyl or cycloalkyl of the acyl group has at least 5 carbon atoms, e.g., the hexahydrobenzoyl, isoheptoyl, and undecoyl derivatives of *p*-phenylenediamine are condensed with (VI).[27] Similar and very reddish blues, which can be dyed from a neutral bath, are obtained from (VI) and aminophenyl alkyl or arylsulfonates;[28] (VI) may be condensed with aminophenols and their derivatives and then treated with an alkyl- or arylsulfonyl chloride.[29] Diaminodi- or triphenylmethanes can be condensed with (VI), one mole of (VI) reacting in aqueous solution and two moles in aqueous alcohol; the fastness is higher in the latter case.[30] Condensing (VI) with a dialkylamide of *p*-toluidine-2-sulfonic acid, the pure blue dyes are fast to light, washing, and fulling.[31] Using a *m*- or *p*-aminoaryl alkyl sulfone, the blue dyes have good leveling properties.[32] Blue and green dyes for wool and nylon, fast to light and washing, are obtained by condensing (VI) with diphenyl derivatives such as 4-aminodiphenyl-4′-sulfocyclohexylamide.[33] In the Alizarin Direct Blue A type of dye, an alkylsulfone group (e.g. $EtSO_2$) in the 5-position of the anthraquinone nucleus leads to greener and brighter shades.[34] Dyes containing a cyano group in the 5- or 8-position have been claimed.[35] The presence of an alcoholic hydroxyl group in the benzene ring (e.g. as in the analog of Alizarin Direct Blue A from *o*-aminobenzyl alcohol), or a hydroxyalkoxy group in the 5- or 6-position,[36] improves leveling properties.[37] Level-dyeing character and fastness to light are claimed for the dyes obtained by condensing (VI) with arylamines substituted by dialkylaminoalkyl groups, and among the amines specified, an interesting example is (IX).[38]

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[25] IG, BP Appl. 7917/36.

[26] IG, BP 454,959. See also General Aniline and Film, USP 2,453,100; 2,453,104; BP 639,660; 639,662.

[27] IG, BP 521,800.

[28] IG, BP 517,396.

[29] IG, BP 505,546.

[30] IG, BP 342,667; 481,897.

[31] Sandoz, BP 421,632.

[32] IG, BP 401,132.

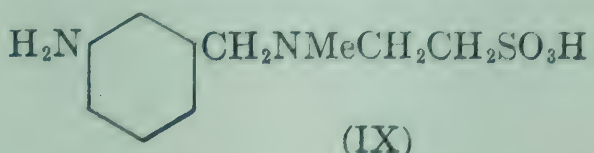
[33] Kern and Allied Chemical and Dyestuff, USP 2,430,771. See also Vogt, USP 2,499,431.

[34] Klein and du Pont, USP 2,176,630.

[35] Buxbaum and du Pont, USP 2,180,336–7.

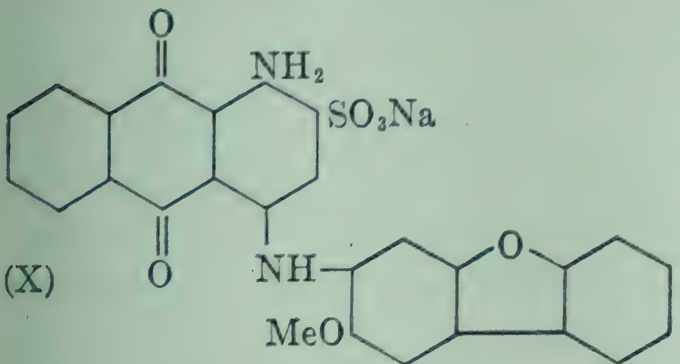
[36] Klein and du Pont, USP 2,179,217.

[37] Wuertz, Klein, and du Pont, USP 2,329,809.

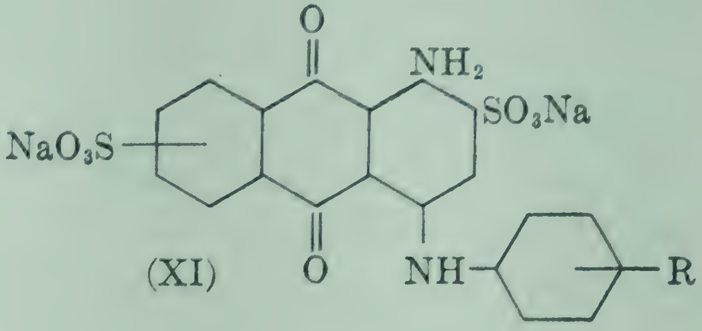


(IX)

Blue to green dyes (e.g. X) for wool and nylon are obtained by heating (VI) with various heterocyclic amines, such as 2-amino-3-methoxydibenzofuran and aminocarbazoles.[39]



(X)



(XI)

Dyes which have a sulfonic group in position 6 or 7, instead of the 2-position or in an aryl residue, are prepared by condensing 4-halogeno-1-hydroarylaminoanthraquinone-6- (or 7)-sulfonic acids with aromatic amines; these have excellent leveling properties and are greener in shade than isomeric products with the sulfonic group in an aryl residue.[40] Blue and greenish blue acid colors of the type (XI) for wool and nylon, which may be prepared from 1-amino-2,4-dibromoanthraquinone-6- or 7-sulfonic acid or from 1-amino-4-bromoanthraquinone-2,6- (or 7)-disulfonic acid, are free from the defect of changing shade in artificial light, which is a defect of some of the dyes described in earlier Sandoz patents. In (XI) R = acylamido, halogen, etc.[41] Great brilliance and good fastness to light are claimed for the dyes made by condensing the 6- or 7-sulfonic acid of (VI) with aminohydroaromatic bases.[42] Fastness to light and wet treatments is claimed for similar dyes from the 5- and 8-sulfonic acids of (VI).[42a] 4-Halogeno-1-aminoanthraquinone-2-sulfonic acids having a sulfonamide group in position 6 or 7 interact with amines to yield blue or blue-green wool dyes with excellent light fastness and good leveling properties.[43]

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[38] Zerweck, Heinrich, and General Aniline and Film, USP 2,333,137.

[39] Kern, and Allied Chemical and Dyestuff, USP 2,407,704; BP 610,808.

[40] IG, FP 794,603.

[41] Sandoz, BP 580,351–2; USP 2,412,790. See also SP 238,265–74.

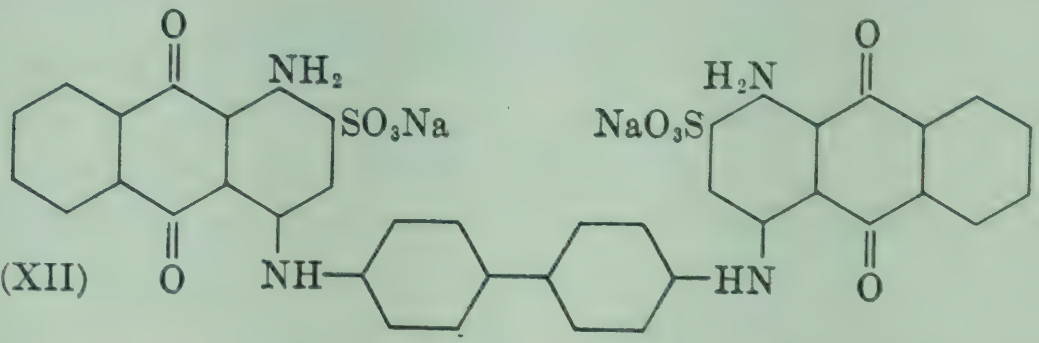
[42] Sandoz, BP 602,419. See also SP 246,258; 251,283–91; 261,859–63; USP 2,453,285.

[42a] Sandoz, BP 630,525. See also BP 630,592; SP 257,724; 259,730–8.

[43] IG, BP 444,904.

Dyes of the type of (XII) are blue, violet and brown wool dyes of excellent light fastness, and the method of preparation which is claimed is the oxidation of Alizarin Direct Blue A with manganese dioxide and sulfuric acid.[44] Nitration of the initial product gives gray dyes.[45] Condensation of Alizarin Direct Blue A with formaldehyde gives the diphenylmethane derivative, which is stated to be fast to light and potting.[46] The condensation product of (VI) with 4,4′-diaminostilbene-2,2′ (or 3,3′)-disulfonic acid dyes nylon and wool from a neutral bath, but not cotton.[46a] Gray dyes for wool are obtained by sulfonating dianilinodianthrimides substituted in the phenyl ring by methyl and having nitro or amino groups in the anthraquinone nucleus.[47] Sulfonated diarylaminotrianthrimides and triaminodianthrimides are claimed as gray dyes of good fastness.[48] The condensation products of 1-amino-4-arylaminoanthraquinones (2 moles) with 3,9-dihalogenobenzanthrones are gray dyes for wool.[49]

(XII)



The unsulfonated 1,4-dialkylaminoanthraquinones (e.g., the di-*n*-amyl compound) are useful for coloring petrol, and sulfonation gives blue acid dyes.[50] Sulfonated 4-arylamino-1-dimethylaminoanthraquinones are greener in shade than the corresponding monoalkylamino compounds.[51] Sulfonated 1,4-bis-polymethylphenylaminoanthraquinones[52] have the defect of reddening in artificial light, but this can be remedied by introducing a halogen atom in the 6- or 7-position.[53] 1,4-Bis-(2′,4′,6′-triethyl)anilinoanthraquinone-2-sulfonic acid is a blue dye suitable for dyeing wool from neutral solution.[54] Outstanding fastness to light and washing is claimed for the bright greenish blue dye prepared by sulfonating 1,4-di-*trans*-2′-benzylcyclohexylaminoanthraquinone.[55] 1,4-Diaminoanthraquinones become brown dyes if one amino group is acylated, and the other is a *p*-benzeneazoanilino group.[56] Sulfonated 1,5-bis(*N*-methylbenzamido)-4,8-bis(*p*-phenylazoanilino)anthraquinone dyes wool from an ammonium acetate bath in shades of exceptional fastness to light and wet treatments.[56a]

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[44] Sandoz, FP 785,494.

[45] Sandoz, BP 419,990.

[46] Sandoz, FP 777,164.

[46a] Vogt and General Aniline and Film, USP 2,476,642.

[47] Buxbaum and du Pont, USP 2,332,779.

[48] Buxbaum and du Pont, USP 2,335,643; Smyth and American Cyanamid, USP 2,454,679.

[49] Buxbaum and du Pont, USP 2,293,709.

[50] Flaks and American Cyanamid, USP 2,205,191.

[51] Whelen and du Pont, USP 2,302,823.

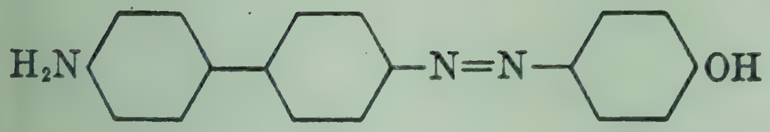
[52] Sandoz, BP 494,802.

[53] Sandoz, BP 560,164. See also SP 222,151–6.

[54] Klein, Perkins, and du Pont, BP 579,519.

1-Amino-4-arylaminoanthraquinones in which the aryl group is a sulfosalicylic acid residue yield green to gray chromium lakes of great fastness to light and washing.[57] When the sulfonic group is in the anthraquinone residue, the products dye blue, green and gray shades as chrome colors; and some of the dyes are suitable for conversion into chromium complexes of the Neolan type.[58]

An interesting development in this class of dye is the attempt to impart affinity for cotton and other cellulose fibers. The azo group appears to be favorable, and the olive or green wool dyes obtained by condensing (VI) with aminoazo compounds have some affinity for cotton.[59] Adequate technical substantivity for cotton is found in the green dye obtained by condensing (VI) with the monoazo dye (XIII). The dyes obtained from 4-aminodiphenyl and its derivatives give fast to light greenish blue shades on cotton and viscose.[60] Using monocinnamoyl-*p*-phenylenediamine, the product dyes bluish green shades on viscose.[61] Products obtained by condensing (VI) with one mole of a compound such as benzidine or diaminobenzophenone, and then acylating with an acid such as cinnamic acid, are greenish-blue dyes with "excellent fastness properties" and with affinity for cotton.[62] Direct cotton dyes (XIV), which dye bluish shades from neutral or alkaline baths, are



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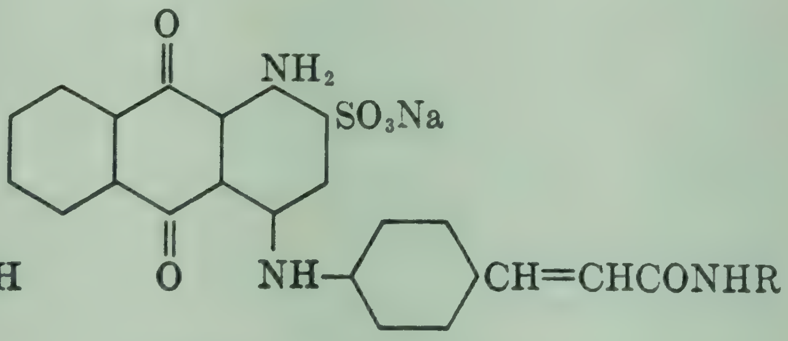

(XIV)

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[55] Buckley, Piggott, and ICI, BP 564,859. See also Tatum and ICI, BP 609,585.

[56] ICI, BP 566,988; 604,833.

[56a] Tatum and ICI, BP 621,713.

[57] IG, BP 452,424.

[58] IG, BP 455,711.

[59] IG, FP 811,890.

[60] IG, BP 381,954.

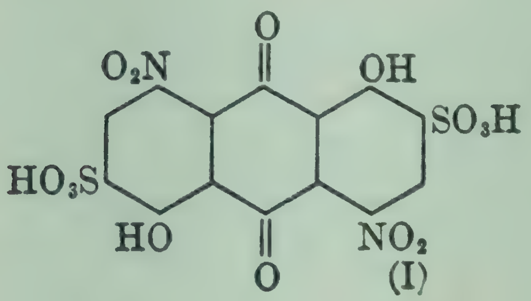
[61] IG, FP 750,329.

[62] Ciba, FP 804,457

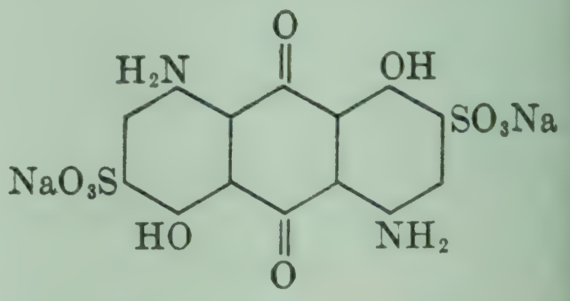
obtained by condensing (VI) with 4-aminocinnamamide and its alkyl and aryl derivatives.[63]

AMINOHYDROXYANTHRAQUINONES

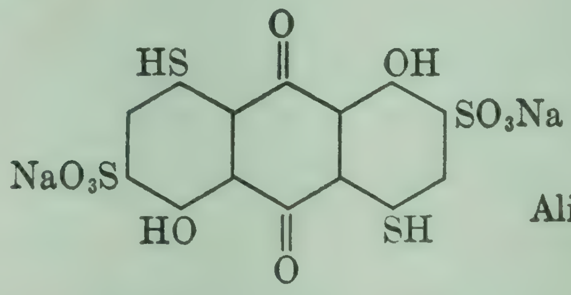
Dyes of this class are prepared by the sulfonation, nitration and reduction of hydroxyanthraquinones; or by the partial replacement of the hydroxyl groups in a polyhydroxyanthraquinone by amino or arylamino groups, followed by sulfonation. The important dyes, Alizarin Saphirol B and SE (By) (Schmidt, 1897), are prepared by the first method. 4,8-Dinitro-1,5-dihydroxyanthraquinone-2,6-disulfonic acid (I) is prepared by the disulfonation and subsequent dinitration of Anthrarufin; reduction with alkaline sodium sulfide gives Alizarin Saphirol B (CI 1054) (Solway Blue B, ICI), a valuable wool dye, giving level reddish blue shades, which by afterchroming become greener and somewhat less bright, and are therefore unsuitable for this treatment although the wet fastness is considerably improved. The unchromed blue shades have high fastness to light (6–7), and the dye is extensively used in spite of its inferior fastness to washing, milling and perspiration. The SE brand (By; CI 1053) is the monosulfonic acid, which may be prepared by the further action of sodium sulfide on Saphirol B, or by the nitration and reduction of Anthrarufin-2-monosulfonic acid; its lower solubility makes it more difficult to apply than Alizarin Saphirol B, but it has better fastness properties, especially to sea water. The bis-*N*-methyl derivative of Saphirol SE is Saphirol SES.[8] Alizarin Saphirol WS is 4,5-diamino-1,8-dihydroxyanthraquinone-2,7-disulfonic acid.[8] When (I) is treated with sodium sulfide successively under alkaline and faintly acid conditions, the nitro groups are replaced by mercapto groups, and the product is Alizarin Emeraldol G (Schmidt, 1905) (By; CI 1056) which dyes bluish green. The dihydroxy derivative of Alizarin Emeral-



(I)



Alizarin Saphirol B



Alizarin Emeraldol G

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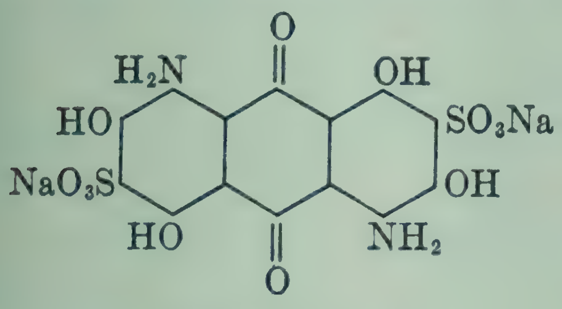
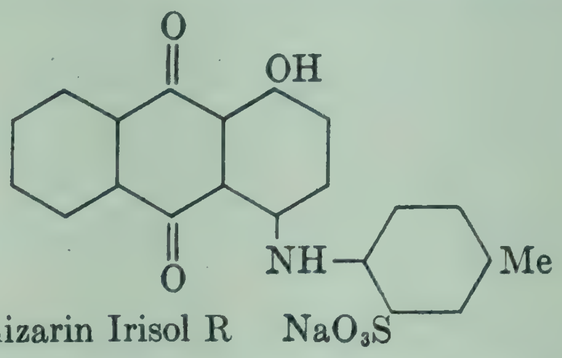
[63] IG, BP 420,688.

dol G is Acid Alizarin Green B (MLB; CI 1049). Acid Alizarin Blue GR (MLB; CI 1048) is prepared by warming Anthracene Blue SWX with 5% ammonia when two α-hydroxyls are aminated, or by the sulfonation, nitration, and reduction of Anthrachrysone.

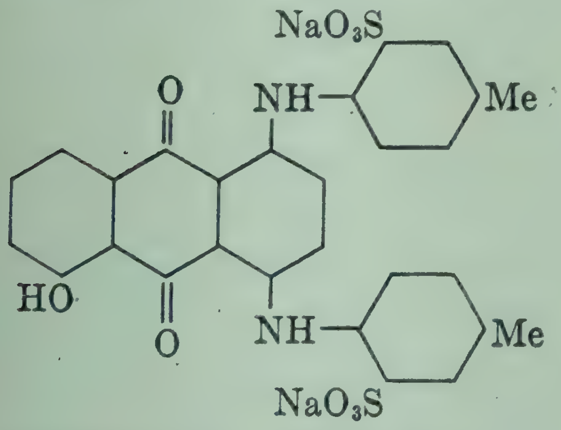
Alizarin Irisol R (Schmidt, 1894) (By; CI 1073) (Anthralan Violet 3B, IG) (Solway Purple R, ICI) is prepared by the same method as Alizarin Cyanine Green, but using conditions under which one molar proportion of *p*-toluidine condenses with leucoquinizarin; 1-*p*-toluidino-4-hydroxyanthraquinone thus formed is then sulfonated. Suitable conditions are to heat Quinizarin (80 kg.), *p*-toluidine (240 l.), hydrochloric acid (35 l.), boric acid (6.75 kg.), zinc dust (3.75 kg.), 90% ethanol (500 l.) and water (33 l.) at 80° until the reaction is complete; sulfonation of the base is carried out by means of 5% oleum at 20–25°.[3, 64] Alizarin Irisol R dyes wool and silk a bright bluish violet from a neutral or acid bath, changed by afterchroming to a greenish blue with excellent fastness properties. The dye is also useful for the preparation of barium and aluminum lake pigments with good light fastness. By heating 1,4,5-trihydroxyanthraquinone, which is prepared from Chrysazin by the action of 80% oleum and boric acid at 30°, with *p*-toluidine, hydrochloric acid, boric acid, and zinc dust at 95°, and sulfonating the product, Alizarin Cyanine Green 3G (Brilliant Alizarin Viridine F) is obtained.[3] Alizarin Cyanine (or Direct) Green 5G (IG), prepared by heating leuco-1,4,5,8-tetrahydroxyanthraquinone with two moles of *p*-toluidine in



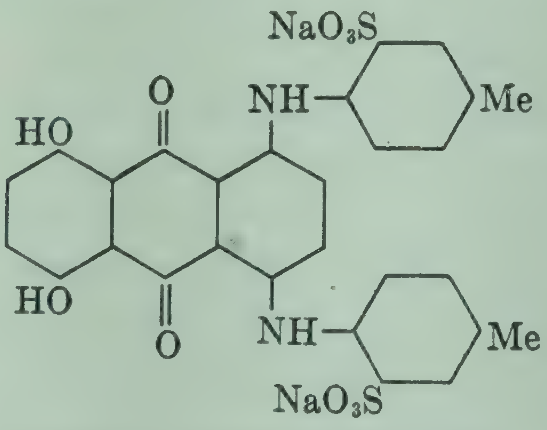
Acid Alizarin Blue GR



Alizarin Irisol R



Alizarin Cyanine Green 3G



Alizarin Cyanine Green 5G

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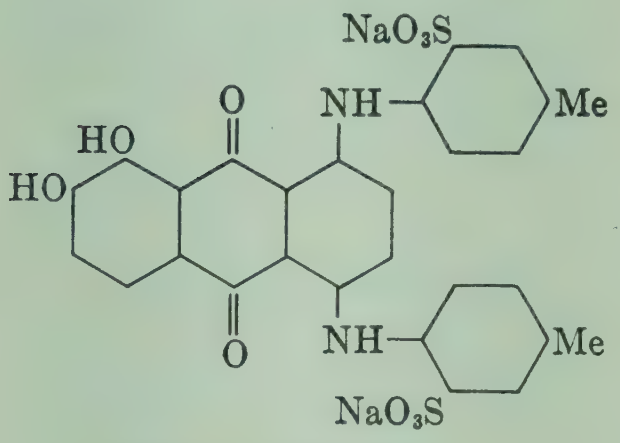
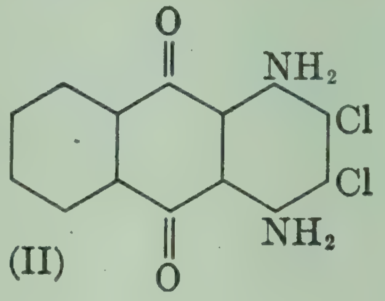
[64] 1-Hydroxy-4-arylaminoanthraquinones are produced in high yield and purity by heating a mixture of Quinizarin, leucoquinizarin, the required arylamine, and boric acid in aqueous alcohol; Klein, USP 2,419,405.

presence of arsenic and boric acids, and sulfonating the product,[3] has excellent light fastness (7–8) and moderate fastness to milling (3). The Alizarin Cyanine Greens can be applied by any of the chrome-development processes, and the milling fastness is thus increased a grade.

Alizarin Viridine FF (Schmidt, 1894) (By; CI 1084), which dyes green on chromium mordant, is prepared by heating Alizarin Bordeaux B (1,2,5,8-tetrahydroxyanthraquinone)[4] with *p*-toluidine in presence of zinc dust, hydrochloric acid and boric acid at about 90°, followed by sulfonation.[3]


Alizarin Viridine FF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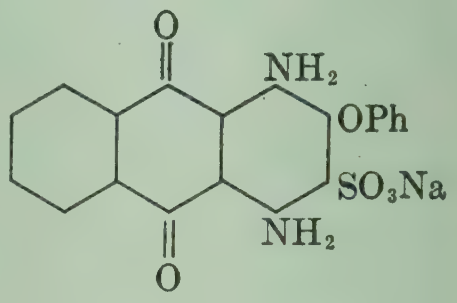
Anthralan Violet 4BF

Anthralan Violet 3R and 4BF are interesting dyes which contain phenoxy groups; they dye clear violet shades and are prepared from 2,3-dichloro-1,4-diaminoanthraquinone (II). For the 3R brand (1,4-diamino-2,3-diphenoxyanthraquinone sulfonic acid), (II; one part) is heated with phenol (6.25 parts) in presence of potassium carbonate at 165–198° for 10 hours, and the product is sulfonated with 1–2% oleum. The 4BF brand is prepared by heating (II) with phenol (5.5 parts), sodium sulfite (3), manganese dioxide (0.25) and water (10) at 140° in an autoclave.[3] Bright reddish violet dyes, which dye wool from an ammonium acetate bath in shades of excellent fastness to wet treatments and good fastness to light, are obtained by sulfonating the condensation product of 2,3-dichloro-1,4-diaminoanthraquinone with the sodium salt of *p*-hydroxydiphenyl or 3-hydroxydibenzofuran.[65]

The absorption spectra of Toluidine Green (Alizarin Cyanine Green 5G), Toluidine Blue, homologs of the latter, analogous compounds containing substituents in the 6,7-positions, and the isomeric 3′-sulfonic acids, have been examined.[66] The effect of changing the position of the sulfonic groups from 2′ to 3′ is a fall in the absorption curve in the far red; and the influence of the position of the sulfonic group in these dyes, as well as a wider range of acid anthraquinone dyes, has been related to the possibilities of hydrogen bonding. Halogen atoms and hydroxyl groups in α-positions have a much greater effect on the absorption curves of this type of dye than the same substituents in β-positions. In connection with their work on the constitution of Toluidine Blue and Green, Allen, Frame and Wilson have developed procedures for reductive and oxidative hydrolysis which should be useful for degradations in the anthraquinone series.[66]

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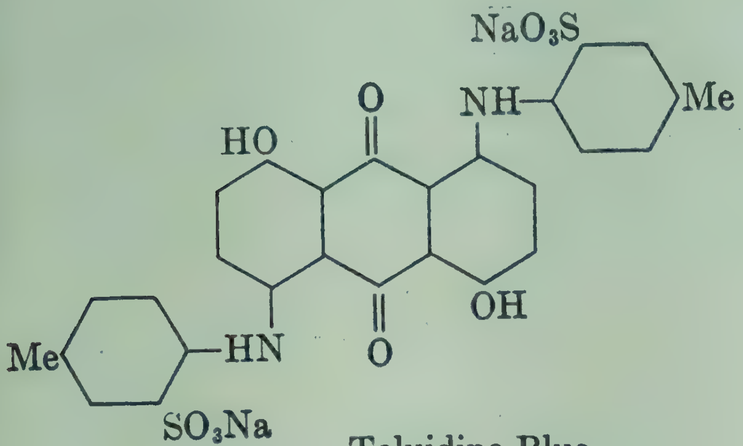
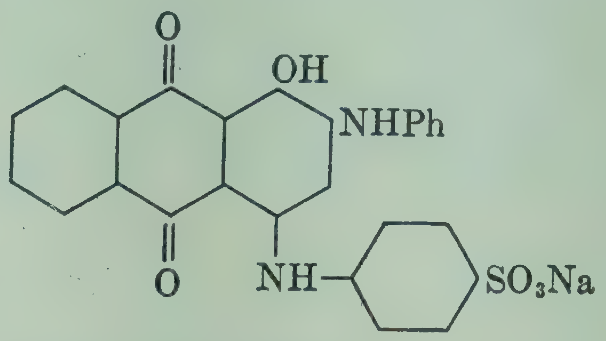
[65] Slinger, Tatum, and ICI, BP 619,034.



Toluidine Blue



Alizarin Blue Black B

By heating Purpurin with aniline in presence of boric acid at 160° for a few hours, the β-hydroxyl and one of the α-hydroxyls are replaced, and the dye obtained by sulfonation is Alizarin Blue Black B (By; CI 1085) (Solway Blue Black B, ICI), which is probably the indicated monosulfonate.[2] The unsulfonated compound can also be prepared by condensing 2-bromoquinizarin with aniline. Alizarin Blue Black B, discovered by Schmidt in 1894, has continued to be a very valuable and largely used dye for fast gray and black shades on wool. Nitration of Alizarin Blue Black B yields Alizarin Fast Black T (IG).[3]

When 4-bromoalizarin-2-sulfuric esters are condensed with arylamines and sulfonated, the products yield blue-green, gray or black shades by afterchroming.[67] The analog of Alizarin Light Grey 2BL prepared by sulfonating 4-amino-4′-hydroxy-1,1′-dianthrimide gives fast bluish gray shades.[68] It has also been reported in a much earlier patent that sulfonated 1,1′-dianthraquinonylamines containing 4-amino and 4′-hydroxy groups are gray to black wool dyes faster to light than the corresponding dihydroxy compounds.[69] Chrome colors are obtained by the introduction of salicylic acid residues. Thus 3-amino-2-hydroxy-5-sulfobenzoic acid is condensed with 2,4-dichloro-1-hydroxyanthraquinone to produce a reddish blue afterchrome dye, and with 4,8-dichloro-1,5-dihydroxyanthraquinone to produce a blue dye which becomes green on chroming.[70]

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[66] Allen, Frame, and Wilson, *J. Org. Chem.* **6,** 737 (1941); **7,** 63, 68, 169 (1942).

[67] IG, GP Anm. J. 52,935.

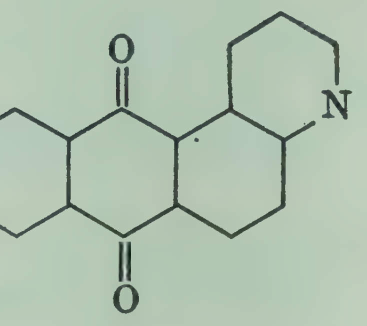
[68] Wuertz, Whelen, and du Pont, USP 2,310,143.

[69] Sandoz, GP Anm. J. 46,554.

[70] IG, BP 482,130; 483,313; 491,862.

Heterocyclic Derivatives

Heterocyclic ring systems derived from anthracene, which are encountered in acid and vat dyes, belong to three main types, and it is convenient to refer to them by trivial names, illustrated by the following: (1) Compounds in which a heterocyclic ring is fused to the 1,2- or 2,3-positions of anthraquinone; e.g., 2,1-pyridino-anthraquinone (I) and 1,2-imidazolo-anthraquinone or anthraquinone-imidazole (II). (2) Compounds in which anthrone is fused in the 1,9-positions to pyridine, pyrimidine, thiazole, pyrazole, etc.; e.g. pyrimidanthrone (III) and pyrazolanthrone (IV).



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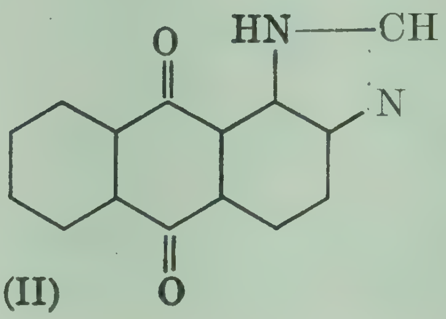

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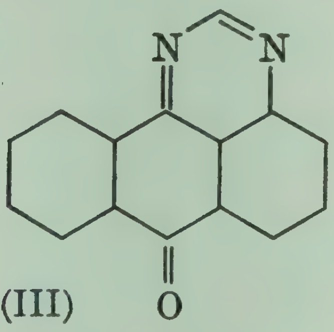

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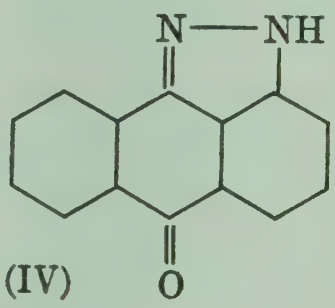
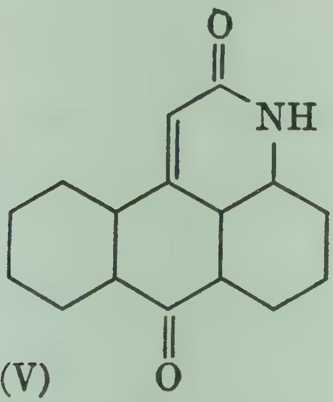
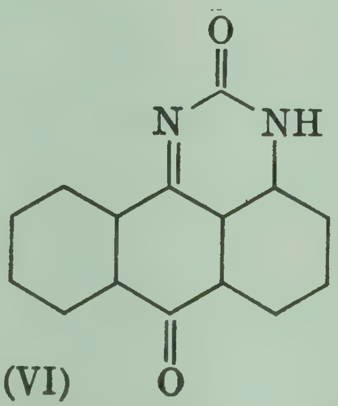


(IV)

(3) Compounds in which anthrone is fused in the 1,9-positions to a pyridone or pyrimidone ring; e.g. anthrapyridone (V) and anthrapyrimidone (VI).

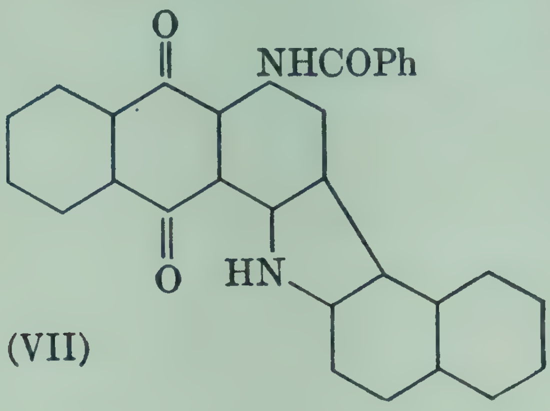


(V)



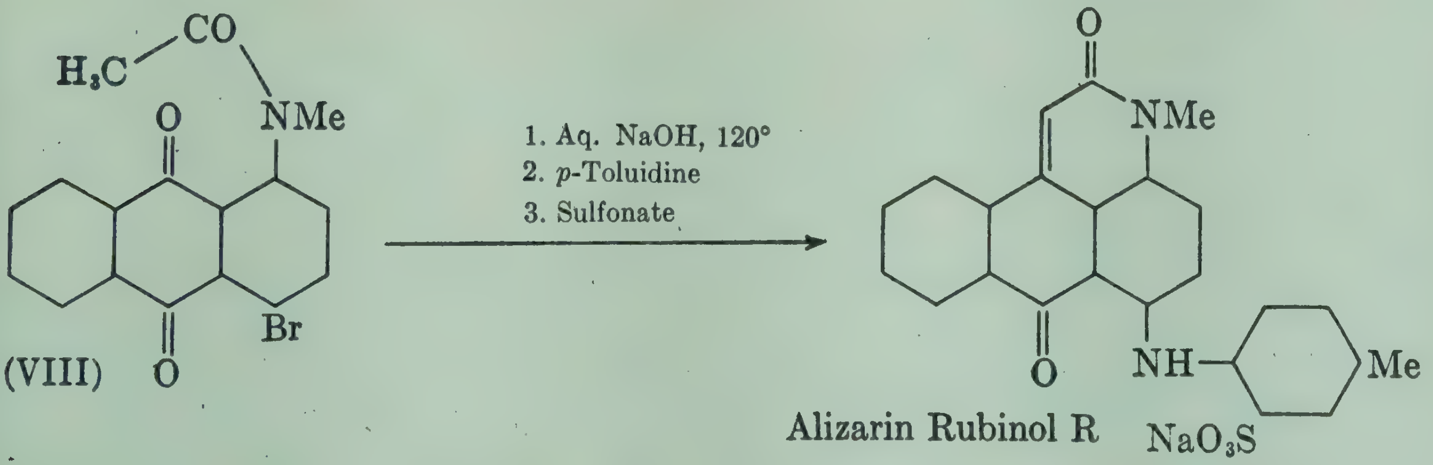
(VI)

Anthraquinone derivatives. When Alizarin Blue (pyridinoalizarin)[4] is submitted to the prolonged action of 70% oleum, the Bohn-Schmidt reaction and sulfonation both take place, and acid-mordant dyes such as Alizarin Green X (BASF; CI 1071) and Alizarin Blue-Green (mainly monosulfonic acids of hydroxy- and dihydroxy-Alizarin Blue) are obtained. These give moderately fast bluish greens on chromium, used at one time for wool dyeing and calico printing. When 1-benzamido-4-β-naphthylaminoanthraquinone is dissolved in concentrated sulfuric acid, the product is a sulfonic acid of the carbazole (VII), and it dyes wool in red-brown shades.[71] If 5-chloro-4-amino-1-benzamidoanthraquinone is condensed with β-naphthylamine, and the resulting naphthylaminoanthraquinone is treated with oleum, it is cyclized to the carbazole and sulfonated in one operation, and such products are gray wool dyes.[72] A fast brown dye, probably a sulfonated carbazole, is obtained by the action of oleum on 1-benzamido-4-*p*-benzeneazoanilino-2-methylanthraquinone.[73]



(VII)

Anthrone derivatives. The more valuable heterocyclic compounds of this group are 1,9-derivatives of anthrone; and their special interest lies in the shades. While the acid and acid-mordant anthraquinone dyes are largely blue, green, gray and black dyes with a few exceptions such as sulfonated Alizarin, red and other shades are available among these anthrone derivatives. An important example is Alizarin Rubinol R (Thomaschewski, 1907) (By; CI 1091) (Anthralan Red 3B, IG) (Solway Rubinol R, ICI), which dyes red shades on wool and silk with light fastness 6 and milling fastness 2–3. It is prepared from (VIII), which is cyclized to the anthrapyridone by means of boiling caustic soda solution; bromine is then replaced by the *p*-toluidino group and the product is



(VIII)

Alizarin Rubinol R

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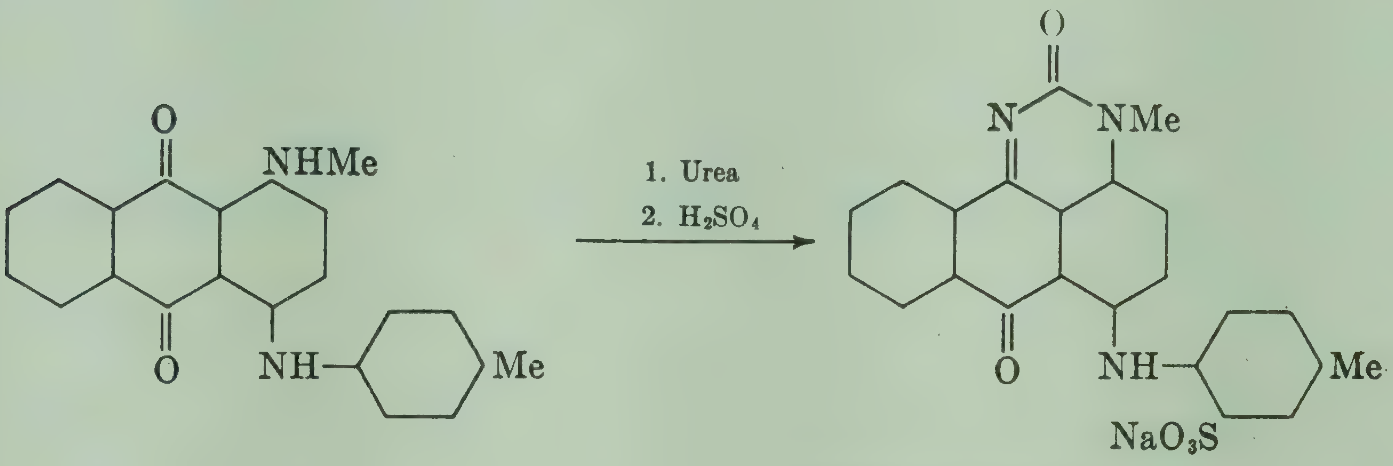
[71] Sandoz, FP 752,280. See also ICI, Lodge and Stephen, BP 607,328.

[72] Lulek, Buxbaum, and du Pont, USP 2,318,174.

[73] Lowe, Robson, and ICI, BP 560,988; Lodge, Wardleworth, and ICI, BP 635,955.

sulfonated. Further sulfonation of Alizarin Rubinol R gives Rubinol GW. Replacing *p*-toluidine by aniline and *m*-chloroaniline respectively in the preparation of Alizarin Rubinol R, the products are Anthralan Red BBT (IG) and Alizarin Rubinol 5G (IG); the latter has been stated to be a disulfonic acid.[8] Alizarin Rubinol 3G is prepared by the further sulfonation of Anthralan Red BBT.[3] Several 3-azabenzanthrone or anthrapyridone dyes, which carry substituents in the 1-position and are not particularly fast to light, have been recently described.[73a] Sandoz[74] prepare anthrapyridones by the condensation of ethyl malonate or acetoacetate with 1-aminoanthraquinones. The replacement of the *N*-methyl group in Alizarin Rubinol R by an aryl group leads to improved fastness to perspiration.[75] Alizarin Geranol B (By, 1912) (Alizarin Astrol Violet B, IG) is a reddish violet dye containing a pyrimidone ring; condensation of 1-*p*-toluidino-4-methylaminoanthraquinone with urea in boiling phenol gives an anthrapyrimidone, which is then sulfonated.[76] The bright heliotrope shades on wool and silk are rendered bluer and faster by afterchroming.



Alizarin Geranol B

While these heterocyclic derivatives of anthrone carry sulfonic groups in attached aryl residues, a type in which the sulfonic group is in the anthrone nucleus has been described. An example is the disulfonic acid of (IX), which is a reddish yellow dye.[77]

6-Aminopyrimidanthrone (X) is a useful intermediate from which the yellow vat dye, Indanthrene Yellow 7GK, is prepared. IG have found[16] that remarkably bright orange to red acid dyes (e.g. XI), with very good light and weather fastness, can be prepared from (X) by the

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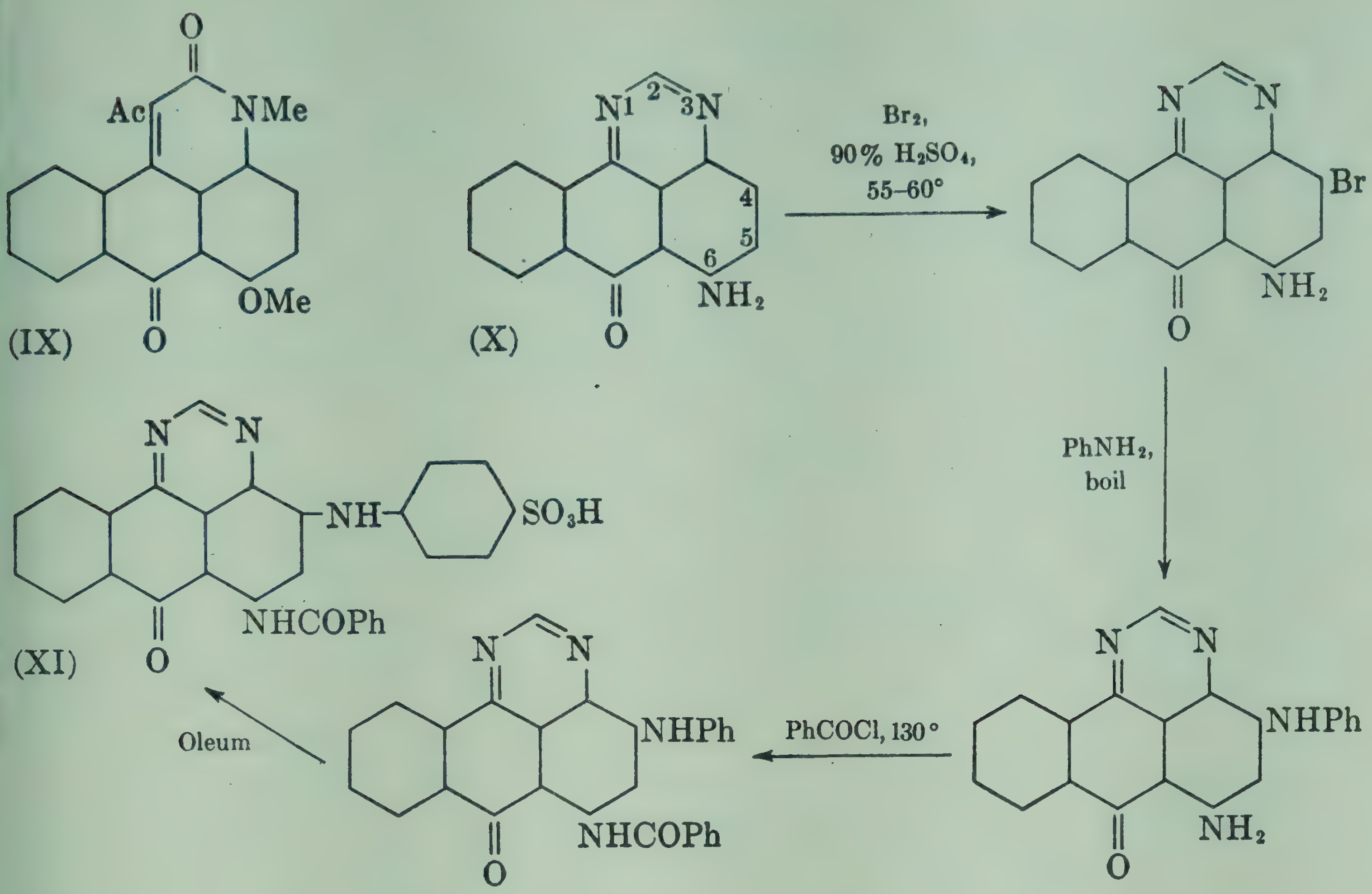
[73a] Allen *et al.*, *JACS* **72**, 585 (1950).

[74] Sandoz, BP 377,632; 380,078.

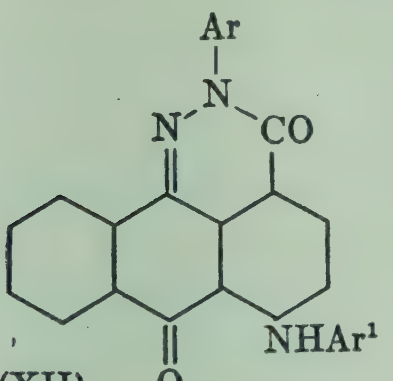
[75] Lodge and ICI, BP 525,091.

[76] IG, BP 393,631; ST 1211 mentions this dye without the *N*-methyl group.

[77] IG, GP Anm. J. **50**, 363.


(IX) (X) (XI)

indicated reactions.[77a] Pyrimidanthrone derivatives are obtained by applying the usual methods for pyrimidanthrone formation to aminoanthraquinonesulfonic acids and yield greenish-yellow dyes.[78] Orange wool dyes are produced by sulfonating the anthrapyridazones (XII). 6-Chloro-2-phenylanthrapyridazone (XIII) is obtained by condensing 4-chloroanthraquinone-1-carboxylic acid with phenylhydrazine.[78a]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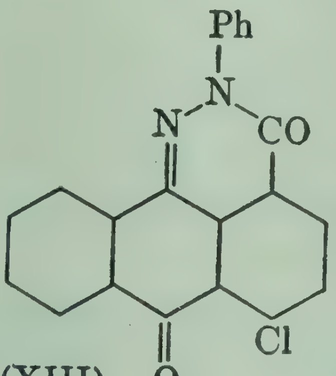
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5-Amino-1,9-thiazolanthrone-3-sulfonic acids yield yellow, orange, red-brown, or violet shades fast to light, and have excellent level-dyeing properties.[79] By condensing 5-halogenopyrazolanthrones with arylamines and sulfonating the aryl group, yellow to orange dyes are obtained.[80]

[77a] See also Wardleworth and ICI, BP 635,104.

[78] IG, FP 767,994.

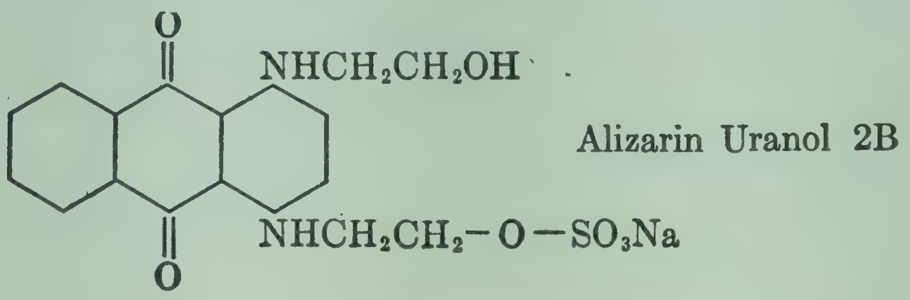
[78a] Coffey, ICI *et al.*, BP 615,837.

[79] IG, GP Anm. J. 53369.

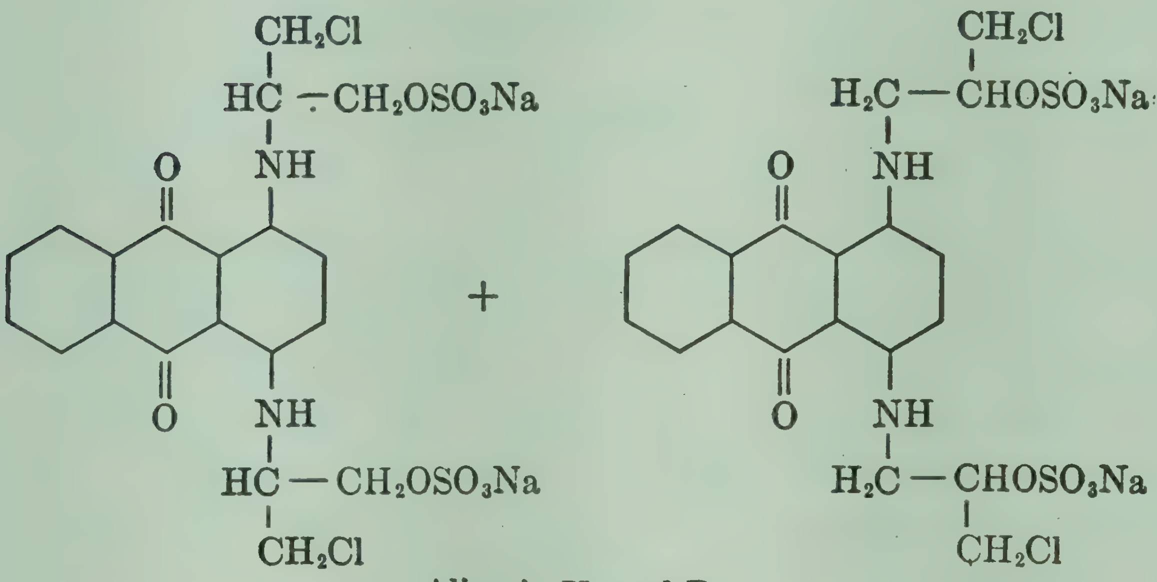
[80] Deinet and du Pont, USP 2,133,432.

ALKYL SULFURIC ESTERS AND SULFONIC ACIDS

Water-soluble sulfuric esters of hydroxyalkylaminoanthraquinones have been described in Chapter XXVII as dyes for cellulose acetate, and dyes of this type are often applicable to wool and nylon. Two important derivatives of 1,4-diaminoanthraquinone which are sulfuric esters are Alizarin Uranol 2B and R (By; ST 1209) (Berchelmann, 1909).[80a] They are bright blue acid dyes with moderate fastness to light; and are prepared by the sulfation of the condensation products of 1,4-diaminoanthraquinone with ethylene oxide and epichlorhydrin respectively. Alizarin Uranol BB (IG) is the 5-nitro derivative of Uranol R.[8]



Alizarin Uranol 2B



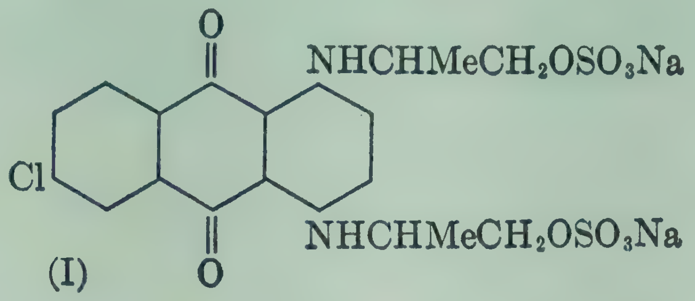
Alizarin Uranol R

Sulfuric esters of 1-amino-4-β-hydroxyethoxyanthraquinones, which may be substituted in the 2-position by halogen, aryloxy, or alkoxy of not more than 5 carbon atoms, are red dyes for wool and cellulose acetate. Sulfuric esters of 1-amino-4-alkylaminoanthraquinones, in which the alkyl group is $-CH(CH_2R)-R'-OH$ (R being H or alkyl, and R′ an alkylene group), dye wool in bright bluish violet shades.[81] When Quinizarin is condensed with hydroxydimethylamine ($NHMe-CH_2OH$) so as to replace both the hydroxyl groups, and the bis-hydroxyalkylaminoanthraquinone is sulfated, the product is a blue, light-fast, level dye.[82] Quinizarin derivatives substituted by chlorine in the 6 or 6,7-positions lead to acid colors which are fast to light and which do not undergo a change in shade towards red in artificial light. An example is (I) which dyes wool a very brilliant blue.[83]

[80a] Bayer, DRP 218,571; 220,627; 235,312. See also Ref. 8.

[81] Tatum and ICI, BP 557,456; 558,433; USP 2,415,377.

[82] Lodge, Lowe, Tatum, and ICI, BP 546,383.



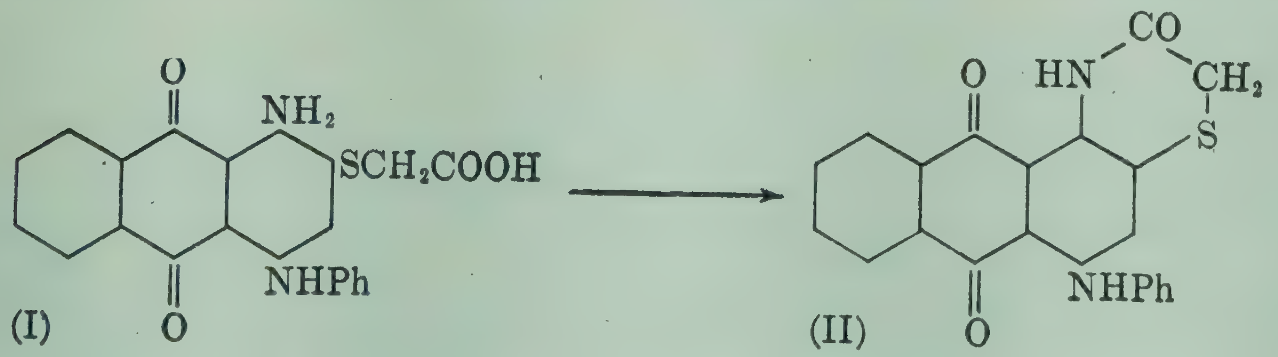
(I)

Blue dyes with good fastness and leveling properties, which are derivatives of 2-methylanthraquinone-ω-sulfonic acid, have been described. These are prepared by the replacement of the ω-chlorine substituent in 1-chloro-2-chloromethylanthraquinone by the SO_3Na group, treatment with ammonia or an amine, bromination in the 4-position, and condensation with an arylamine.[84]

Aminoanthraquinonesulfonic acids can be converted into the sulfonyl chlorides by means of phosphorus pentachloride without affecting the amino groups.[85] Sulfonamides may thus be prepared readily from 4-bromo-1-aminoanthraquinone-2-sulfonic acid, and further condensation with aromatic amines containing sulfonic groups provides another extension of the range of acid anthraquinone dyes. The amine used for the condensation with the sulfonyl chloride may be a sulfonic acid such as *N*-methyltaurine ($NHMe{-}C_2H_4{-}SO_3H$), and the 4-aryl residue then need not carry a sulfonic group.[86] Mercaptoanthraquinones react with halogenoalkylsulfonic acids to yield products dyeing yellow, violet, blue or gray shades according to the other substituents present.[87]

Dyes with High Fastness to Milling and Potting

Two types of wool dyes discovered by ICI (1931–1933) which are characterized by excellent fastness to severe wet treatments contain *o*-aminothioglycolic acid or heavy alkyl groups. These two devices can be employed in the anthraquinone as well as the azo series (see Chapter



(I) (II)

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[83] Sandoz, BP 571,673; USP, 2,386,309; SP 229,186; 234,787; 234,950–1.

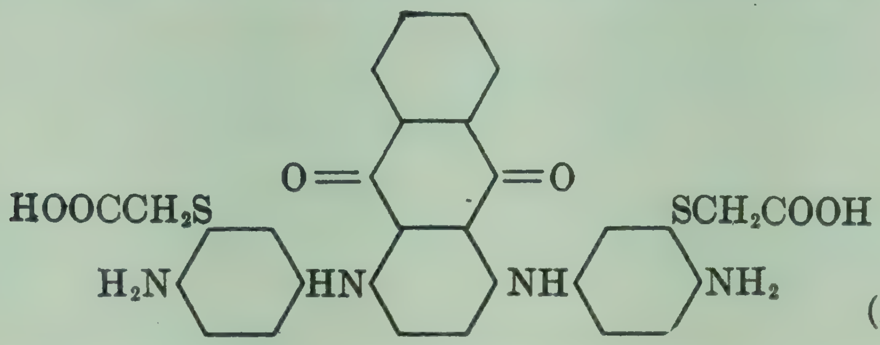
[84] IG, GP Anm. J., **49**, 887.

[85] IG, BP 397,190.

[86] IG, BP 399,095.

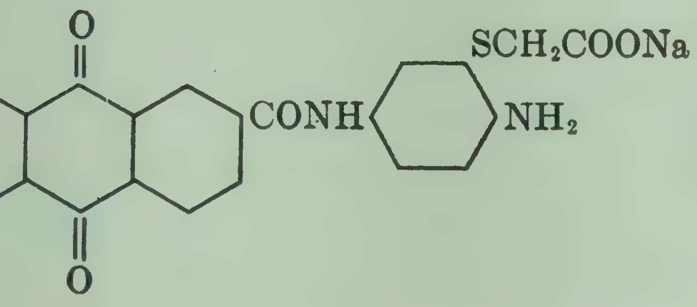
[87] IG, BP 461,998.

XI). In the first method an aminoanthraquinone is solubilized by the introduction of a thioglycolic acid group in an adjacent position; when the dye (I) is applied from an ammonium acetate bath and treated on the fiber with hot dilute acid, cyclization to the insoluble lactam (II) takes place.[88] The resulting shades are exceptionally fast to potting.

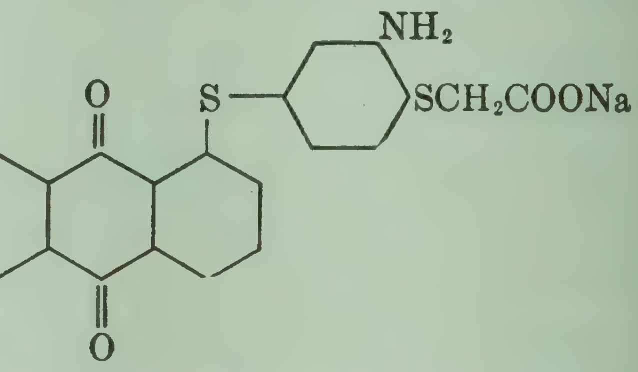


(III)

A wide range of shades is obtainable by varying the substitution. For deep shades, the amino groups attached to the anthraquinone nucleus should not be involved in lactam formation (cf. III). Compounds in which the anthraquinone nucleus is linked to the lactamizing residue by a CONH or NHCO group (e.g. IV) yield yellow, orange, and scarlet shades.[89] By modifying the process the methylene group of the thioglycolic acid residue may be replaced by —CRR′—, where R and R′ may be hydrogen or alkyl;[90] and in a further series (V) giving slightly deeper shades, the link between the anthraquinone and the lactamizing residue is formed by a sulfur atom.[91]

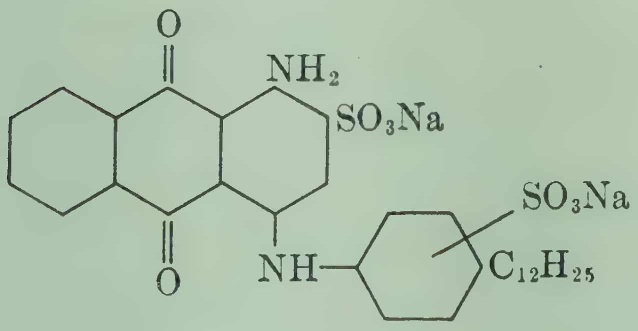


(IV)

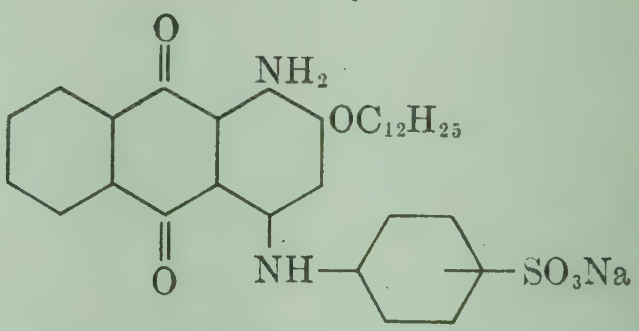


(V)

In the second method, one or more alkyl groups (C_4 to C_{20}) are introduced in anthraquinone acid dyes, belonging to any of the types



Carbolan Blue B



Carbolan Violet 2R

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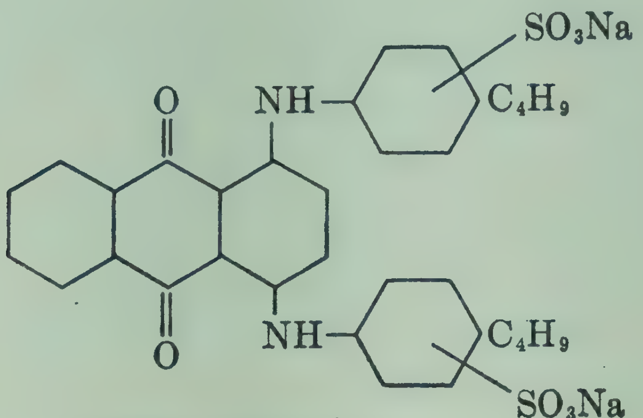
[88] Haddock, Lodge, Lumsden and ICI, BP 377,740; 394,312.

[89] Haddock, Lodge, Lumsden, and ICI, BP 406,689; 406,733.

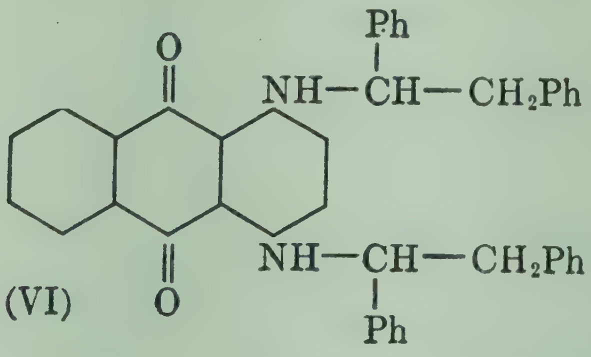
[90] Haddock, Lodge, Lumsden, and ICI, BP 413,658.

[91] ICI, BP 412,920.

discussed earlier, and several members of the Carbolan class (ICI) (e.g. Carbolan Violet 2RS, Blue BS and RS, and Green GS) are thus constituted.[9, 92] The long chain alkyl group may be on a nuclear carbon atom, or may be attached to oxygen as an ether or ester, or to nitrogen or sulfur. While the presence of the alkyl group has a marked influence on the fastness to milling and potting, the color of the dye is but little affected. 1-*iso*Amylamino-4-(*p*-*n*-butyl)anilinoanthraquinone yields a bright bluish-green wool dye on sulfonation.[93] The violet to blue dyes obtained by brominating and sulfonating 1,4-*bis*-*p*-butylanilinoanthraquinones, in which one or both *p*-butylanilino groups may carry methyl groups, are fast to severe milling.[94] ICI combine brightness of shade with outstanding fastness to washing, milling, and light in the violet and blue dyestuffs obtained by sulfonating anthraquinone derivatives substituted by secondary amino groups which carry aralkyl or aryl residues. Thus leucoquinizarin is condensed with α,β-diphenylethylamine to obtain (VI), which on sulfonation yields a fast, bright blue dye;[95] *trans*-2-benzylcyclohexylamine can be used for a similar purpose.[96] IG obtain high washing fastness by replacing the arylamino groups in anthraquinone acid wool dyes of the Alizarin Direct Blue A type by



Carbolan Green G



(VI)

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[92] BP 430,160; 437,266; 433,776; 449,010–2; 452,203; 477,535; 483,325; 484,000. See also Harris, Marriott and Smith, *JCS* 1838 (**1936**).

[93] Heslop, Tatum, and ICI, BP 477,293.

[94] ICI, BP 446,819; 514,770; Sandoz, BP 494,802.

[95] BP 491,493; 497,016.

[96] Buckley, Piggott, and ICI, USP 2,426,547.

aminopyrene.[97] Benzanthronylaminoanthraquinones, which are intermediates for vat dyes, have been sulfonated to obtain gray to brown wool dyes, which are particularly fast to acid milling.[98] 1,4-Di-*p*-toluidino-5,6,7,8-tetrahydroanthraquinone, prepared from tetrahydroquinizarin dimethyl ether, yields on sulfonation a green wool dye which has good fastness to washing and fulling,[99] and sulfonation of 1,4-*bis*-*p*-phenoxyanilinoanthraquinones also yields very fast dyestuffs.[100]

The sulfonic group in 1-amino-4-arylaminoanthraquinone-2-sulfonic acids may be replaced by OR, where R contains 8 to 20 carbon atoms, by heating with an alkali-metal derivative of the corresponding monohydric alcohol. After resulfonating (in the arylamino group), violet shades of improved fastness to washing, milling and potting are obtained (cf. Carbolan Violet 2R).[101]

[97] IG, FP 837,558; see also Ciba, BP 514,637.

[98] Sandoz, BP 508,742.

[99] IG, BP 510,010.

[100] Geigy, BP 487,830.

[101] Lodge, Lumsden, and ICI, BP 430,160.

CHAPTER XXX

ANTHRAQUINONE VAT DYES

GENERAL

In an attempt to prepare an anthraquinone analog of indigo, Bohn (1901) studied the cyclization of the condensation product of β-aminoanthraquinone and chloroacetic acid by means of caustic alkali, and obtained a blue dye, which he named indanthrene (a portmanteau word from indigo and anthracene). As the chemical name for Bohn's blue dye, indanthrone is now preferred to indanthrene, since it indicates the quinone structure and distinguishes it from the trade name of the Indanthrenes. Bohn was soon able to show that the alkali fusion of β-aminoanthraquinone itself gave the same product, which was therefore not an indigoid dye. He had synthesized a new class of vat dye, which had the constitution of a dihydroanthraquinoneazine, and this was fully confirmed by the later work of Scholl on indanthrone and its derivatives. With the amalgamation of the German dyemakers into the IG in 1924, Indanthrene was adopted as the group name for vat dyes with the maximum all-round fastness. Bohn's discovery was a landmark in the history of synthetic dyes, as well as the cotton textile industry, since indigo and Tyrian purple were the only vat dyes known during the preceding centuries. The acid anthraquinone dyes and the azo dyes had already provided the wool and silk dyer with an extensive range of fast dyes, but the position in cotton dyeing was very different. With alizarin as almost the only exception, there was a complete lack of fast dyes for cotton; even indigo gave shades on cotton which were inferior in their fastness to the shades on wool. The anthraquinone vat dyes were therefore a development of the utmost importance for the cotton industry. Indanthrene Blue and the series of the anthraquinonoid vat dyes which followed it in rapid succession possessed fastness properties of unsurpassed excellence, representing indeed a degree of permanence often greater than that of the fibers themselves. While the anthraquinone vat dyes in the commercial range undoubtedly represent the highest standard of all-round fastness yet attained among organic coloring matters, it is important to remember that a vat dye derived from anthraquinone is not to be automatically regarded as possessing the highest fastness to all agencies. There are wide variations in the fastness properties of the anthraquinone vat dyes, and the dyes in the commercial range are a relatively small group carefully chosen from among thousands which have been made and examined in the research laboratories of dyestuff manufacturers.

At the present time the anthraquinone vats[1–6] include a wide range of shades from yellow to black, and some of the outstanding examples in chronological order have been cited in Chapter I. The shades produced on cotton by the anthraquinone vat dyes in the early years of their manufacture were inclined to be dull, and to compare unfavorably in this respect with the brilliant basic dyes. Continuous improvements in manufacture, as well as the synthesis of new members of the series, have now made several anthraquinone vat dyes available which are comparable in brightness to Auramine, Crystal Violet, and other basic dyes. There has been continuous improvement in the purity of the intermediates used in the manufacture of the vat dyes; and another factor which has resulted in brighter shades is the development of methods of purification of the dyes themselves, such as separation from sulfuric acid solution and oxidation of the impurities by means of hypochlorite or dichromate. However, the brilliance and intensity of the azoic scarlets and reds and the basic blues and greens have not yet been attained. Fastness considerations justify the use of the anthraquinonoid vat dyes, but as a class they are expensive, especially because many of them (e.g., reds, browns and blacks) have to be used in high percentages on the weight of the yarn for dyeing full shades. In large scale dyeing and printing, the vat dyes present special problems, and although most of these have now been solved, the application of the vat dyes still requires considerable skill. Many yellow and orange vat dyes of the anthraquinone series accelerate the degradation of cellulose by light, and dyes for the production of lemon or greenish yellow shades with the maximum light fastness and complete absence of the tendering effect remain to be discovered.

It has been computed that about a fifth of the world consumption of dyes consists of the anthraquinone vat colors, which therefore occupy a place which is second only to the azo dyes from the commercial point of view. In money value they probably surpass the azo dyes. The prewar IG production of Indanthrenes was of the value of 200 million marks, exceeded only by the azo dyes. The United States production of anthraquinone vat dyes in 1946 was of the value of $47,337,000 which may be

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[1] Bohn, *Ber.* **43,** 987 (1910); *Rev. gen. chim.* **13,** 257 (1910).

[2] Fraser-Thomson in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. I, Longmans, London, p. 404.

[3] Thorpe and Ingold, Vat Dyes, Longmans, London, 1935.

[4] Houben, Das Anthracen und die Anthrachinone, Thieme, Leipzig, 1929.

[5] Kunz, *Bull. Soc. Ind. Mulhouse* 3 (1934); *Angew. Chem.* **52,** 269 (1939).

[6] Kränzlein, Künstlichen organischen Farbstoffe, Ferdinand, Stuttgart, 1935.

compared with the value of $110,748,000 for all the synthetic dyes. Judged in terms of their fastness and their chemical interest as complex polycyclic compounds of varied types, the vat dyes derived from anthraquinone may well be regarded as the most important group among the synthetic dyes. Before the first world war Germany was the only producer of anthraquinone vat dyes, but strenuous efforts since made by Great Britain and the United States have resulted in the large scale production of many of the dyes in both these countries.[7] They are also being manufactured at the present time in Switzerland, France, and Italy, and the Japanese dye manufacturers had launched on the production of a narrow range of anthraquinone vat dyes some years before World War II.

Commercial names.[8] Originally introduced by BASF under the name Indanthrene, other German manufacturers gradually began to market anthraquinone vat dyes under names such as Algol (By) and Vat (GrE); a few of the Helindones (MLB) were anthraquinonoid vat dyes. Ultimately, IG used the term Indanthrene for vat dyes with the maximum all-round fastness; although the great majority were anthraquinone derivatives, a few thioindigoids also found a place (e.g., Indanthrene Magenta B and Indanthrene Brilliant Pink R), and many of the Indanthrene Printing colors belonged to the thioindigoid class. The term Algol was restricted to vat dyes, both indigoid and anthraquinonoid, which were suitable for dyeing cotton in shades with moderate to good fastness (light 4–5; chlorine 3; alkali boil 3–4), but with fastness properties inferior to those of the Indanthrenes; nearly all the Algol colors in the current range are indigoid. The Helindones are vat dyes, mostly indigoid, which are more applicable to wool than to cotton. Caledon is the ICI group name for the anthraquinone vat dyes, but a few are still marketed under the old name Alizanthrene (British Alizarine Co.). The British firm of L.B. Holliday market a large range of anthraquinone vat dyes under the name Paradone. Ciba market the anthraquinone vat dyes, including the sulfurized dyes in the series, under the name Cibanone. Among the names used by other Swiss manufacturers are Tinon Chlorine (Gy) and Sandothrene (S). In the United States GAFC and GDC employ the IG names; the Calco name is Calcoloid; du Pont Ponsol; and NAC Carbanthrene. In this chapter the abbreviated names of firms are not added after the commercial names of the dyes, since the relationships have been explained at this stage, and the bulk of the available information on constitution concerns IG dyes.

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[7] See Morton, History of the Development of Fast Dyeing and Dyes.

[8] Fox, Vat Dyestuffs and Vat Dyeing, Chapman and Hall, 1946, has tabulated the equivalents of vat dyes made by various dye manufacturers.

CLASSIFICATION

The ability of a coloring matter to function as a vat dye depends on two fundamental characteristics: the property of the insoluble dye to vat or form a soluble alkali salt by reduction with an alkaline reducing agent, and the affinity of the leuco salt for textile fibers, especially the cellulose fibers. Oxidation on the fiber, usually with atmospheric oxygen, regenerates the insoluble dye. The vats of the anthraquinone dyes are deeply colored, sometimes deeper than the parent dyes, the vat of the yellow flavanthrone for instance being blue in color; the indigoid dyes give nearly colorless, yellow or pale brown vats. Anthraquinone itself vats with hydrosulfite and caustic soda,[9] but the introduction of certain groups and an increase in the molecular weight are necessary for converting it into vat dyes. With the exception of a few dyes derived from pyrimidanthrone, all the anthraquinone vat dyes contain a pair of carbonyl groups as a 1,4-quinone or as part of a complex quinone system in a polycyclic aromatic compound. From this point of view, the anthraquinone vat dyes fall into two broad divisions: (a) anthraquinone derivatives and (b) anthrone derivatives in which the 1,9-positions are involved in a new ring system. In (a) one anthraquinone nucleus is adequate for producing a vat dye, although most of the technically important dyes contain two or more anthraquinone systems; but in (b), with the exception of the pyrimidanthrones, the anthrone unit has to be doubled in order to produce a vat dye. Further classification may be made on the basis of a characteristic group, such as an acylamido group, the presence of heterocyclic ring systems, the nature of the carbocyclic system, or the use of a common intermediate such as benzanthrone. The present treatment classifies the anthraquinone vat dyes into the following groups:

(A) **Anthraquinone derivatives:** (I) Simple derivatives of anthraquinone: (a) Acylamidoanthraquinones; (b) Cyanuric acid derivatives; (c) Anthrimides; (d) Miscellaneous derivatives, such as dianthraquinonylethylene. (II) Compounds in which a heterocyclic ring is fused to the anthraquinone nucleus in the 1,2 or 2,3-positions: (a) Carbazoles; (b) Imidazoles; (c) Oxazoles; (d) Thiazoles; (e) Acridones; (f) Thioxanthones; (g) Anthraquinoneazines (Indanthrones); (h) Phthaloylquinoxalines.

(B) **Anthrone derivatives:** (I) Carbocyclic compounds: (a) Pyrene and Perylene derivatives; (b) Benzanthrone derivatives; (c) Pyranthrones; (d) Naphthodianthrones and Anthradianthrones; (e) Dibenzopyrenequinones; (f) Anthanthrones; (g) Miscellaneous homocyclic quinones. (II) 1,9-Heterocyclic derivatives: (a) Flavanthrones; (b)

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[9] See Chapter III.

Pyrazolanthrones; (c) Pyrimidanthrones; (d) Anthrapyridones and anthrapyrimidones; and (e) Miscellaneous heterocyclic compounds.

STANDARDIZATION OF ANTHRAQUINONE VAT DYES

The physical form of an anthraquinone vat dye is an important factor which materially influences the ease of vatting and the affinity. A dye which has been separated in crystalline form from an organic solvent can offer considerable difficulty in vatting and lead to poor shades; both the vatting and dyeing properties are markedly improved by dissolving the crystalline dye in concentrated sulfuric acid and precipitating the dye by drowning in water.[9a] In a laboratory preparation the filtered dye should be used without drying, since drying in an oven, or even in the air or in a desiccator, is prejudicial to good vatting and dyeing. Vatting may be further facilitated if necessary by wetting with alcohol or pasting with Turkey Red oil. In technical practice, the dyes go through a process of standardization in which they are not only standardized in their strength or concentration, but are also converted into suitable physical forms for dyeing or printing.[10, 11] The dye, isolated at the end of the chemical reactions for its synthesis, may be dissolved in sulfuric acid and reprecipitated; the shades of many dyes are considerably improved by a treatment with sodium hypochlorite or dichromate solution at about 95° for an hour or more with vigorous mechanical agitation; another procedure is to dissolve the dye in concentrated sulfuric acid containing about 0.2% sodium nitrite, drown in water, add a further quantity of sodium nitrite, and agitate at about 90° for an hour or two. The dye may be vatted and reoxidized; and vat dyes of high tinctorial power may be prepared by adding a surface-active compound, such as an alkylnaphthalenesulfonic acid, to the vat before reoxidation. The filter-press cake is made into an aqueous paste containing about 10% of the dye, mixed with about 2% of a dispersing agent (e.g., a condensation product of an alkylnaphthalenesulfonic acid and formaldehyde, alkali salts of phenylglycine and other amino acids,[12] ethyl hydrogen sulfate and β-ethoxyethyl hydrogen sulfate),[13] and ground in a mill. The paste may then be mixed with water and passed through a supercentrifuge, again agitated in a vat with the addition of more of the concentrated dye paste or of a second dye for adjustment of shade and strength, and finally sieved through fine-mesh screens (100–300 mesh). A Paste Fine brand is more finely divided than a paste brand. In the preparation of Powder and Powder Fine brands, the paste is dried on a drum dryer or by spray drying, mixed with diluents such as sodium bicarbonate, anthraquinone (as a reduction catalyst) and wetting agents, and powdered very thoroughly in a keg mill or micropulverizer. Highly dispersible preparations are made by kneading a vat dye with a protective agent of defined type and a deflocculating agent and, if desired, drying and grinding the paste obtained.[14] Protective agents are defined as the carbohydrate colloids such as dextrin, alkali metal silicates, pectin and colloidal clays. Specified deflocculating agents are tannic acid, sulfonated diarylmethanes, and the sodium salt of disulfodinaphthylmethane; when carbohydrate colloids are used as protective agents they may also act as deflocculating agents. When dispersing agents and diluents such as sulfite cellulose liquor residues and dextrin are added, their retarding action in dyeing must be kept in view. A preparation containing a vat dye in a finely divided state is made by dissolving in a solvent of the group consisting of aliphatic monohydric or polyhydric alcohols and their ethers, aliphatic hydroxy carboxylic acids and esters of such acids, and thiodiglycol, or in a mixture of such solvents, a cellulose derivative, an ester salt of a leuco vat dye and an oxidizing agent, and treating the solution with an acid, preferably an organic acid, whereby the vat dye is reformed in a finely divided state from the ester salt.[15]

[9a] See also Cullinan, Lytle, and American Cyanamid, USP 2,475,821; 2,475,847.

[10] Diserens, The Chemical Technology of Dyeing and Printing, Reinhold, New York, 1948.

[11] *FIAT* **970; 1040.**

[12] Tolman and National Aniline, USP 2,086,831.

[13] Kern and National Aniline, USP 2,145,193.

A process described for producing a vat dye powder with an autodispersive power of 85–90%, giving a practically complete colloidal dispersion in aqueous media or in printing pastes, contains a protective agent, a wetting agent, an antidusting agent and a diluent.[16] A simple and effective method of producing vat dyes in a very highly dispersed form is to oxidize a solution of the leuco salt or the leuco sulfuric ester in presence of a protective colloid.[17] A novel method of producing a vat dye gel suitable for dyeing cotton is to dye wool with the vat dye from a hydrosulfite-alkali vat, dissolve the dyed wool in alkali, and acidify.[18]

For use in calico printing the vat dyes must be in a specially fine state of division, and special printing brands are often marketed. These may contain solvents such as diethylene glycol or various substances which improve the solubility, assist the vatting process, increase penetration, and produce higher color value as well as brighter, clearer prints. Among

[14] Crossley, Kienle, Royer, and Calco, BP 474,827.

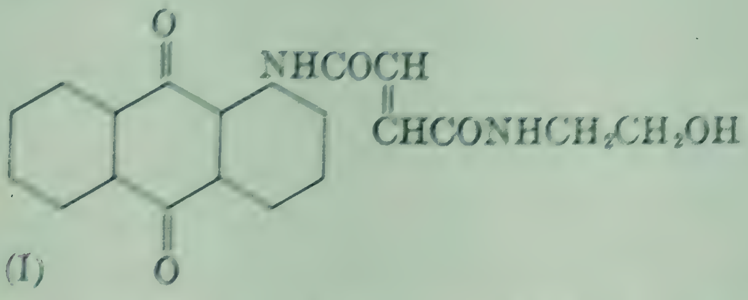
[15] Durand and Huguenin, BP 560,747.

[16] Calco, FP 804,300.

[17] Morton and Courtaulds, BP 485,466.

[18] Child, Thomas, and ICI, USP 2,081,736.

any examples may be mentioned sodium benzoate; sodium monobenzyl-
r dibenzylsulfanilate; sodium alkyl phosphates;[19] sodium alkyl sulfates
f specified types; sodium salts of α-methylvaleric, γ-methylhexoic and
imilar acids, thioglycolic acids such as $PhMe_2C–S–CH_2COOH$, mono-
enzyl or monoalkyl phthalate,[20] o-benzoylbenzoic acid and other ketone
arbozylic acids or sulfonic acids;[21] α-aminoacids ($RNHCH_2COOH$, in
hich R = H, Me or Ph);[12] alkyl carbamates;[22] o-hydroxybenzyl
lcohol;[20, 23] p-hydroxyphenylphthalide;[24] N-1-anthraquinonyl-N′-etha-
olfumaramide (I);[25] and polyethylenepolyamines (e.g., $NH_2–CH_2CH_2–$
$H–CH_2CH_2–NH_2$).[26]


(I)

The Suprafix dyes (IG) consist essentially of mixtures of a vat dye (sometimes as the leuco compound), sodium benzylsulfanilate (Solution Salt B), and a booster (such as 2,6-dihydroxyanthraquinone or ferrous sulfate).[26a] A typical procedure for the preparation of a Suprafix is to mix in a lead-lined vessel glycerol (30 parts), Solution Salt B (10), ferrous sulfate (2.5), 6.5% gum tragacanth solution (10), Preventol (an antiseptic to prevent mold formation and putrefaction), and the dye (10); the mixture is then worked in a colloid mill and sieved.

Vat dye pastes are usually 10% in strength, a "double paste" being 20%. The powder brands are of the order of 50% in strength, but wide variations may be encountered. The dyer prefers powder to paste brands since the former is easier to handle and weigh. Paste brands are also difficult to store; the paste may dry up partially and the product may become heterogeneous in its dye content, so that intimate mixing will again be necessary before use. The present tendency therefore is to market powder brands, but in such a fine state of division that they disperse very readily in water.

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[19] IG, BP 508,554.

[20] du Pont, USP 2,069,215; 2,173,824; 2,174,486; 2,205,032.

[21] Kern and National Aniline, USP 2,074,150.

[22] Kienle and Amick, USP 2,421,622.

[23] du Pont, USP 2,079,788.

[24] Weiland and Stallman, USP 2,078,866.

[25] Kienle, Amick and American Cyanamid USP 2,371,103.

[26] Clark and Allied Chemical and Dyestuff, USP 2,286,262.

[26a] Diserens, *Teintex* **2**, 341, 407, 475 (1937); USP 2,069,215. See also Berthold, *Melliand Textilber*, **31**, 422 (1950).

General Properties and Reactions

The anthraquinone vat dyes are in general difficult to obtain in analytically pure condition because of their high molecular weight and sparing solubility in organic solvents; since few of them have melting points and most only decompose at high temperatures, there is no simple method by which the purity of a vat dye can be determined. The treatments mentioned earlier in connection with standardization, such as precipitation from sulfuric acid, vatting and reoxidation, and oxidation with sodium hypochlorite or with dichromate and sulfuric acid, are obviously useful also as methods of purification. The sparing solubility of the anthraquinone vat dyes in the common organic solvents may be utilized for removing the intermediates from which the dyes were synthesized and by-products of relatively low molecular weight and greater solubility. Many of the anthraquinone vat dyes are crystallizable from high boiling solvents such as nitrobenzene, *o*-dichlorobenzene, trichlorobenzene, phenol, cresols, *o*-chlorophenol, and quinoline. Large volumes of solvents and suitable arrangements for hot filtration of the toxic solvents are necessary. If impurities have been largely removed by prior treatments and the object is to produce the dye in crystalline form, the dye may be refluxed for a few minutes with a limited amount of a solvent, such as trichlorobenzene, and left to cool; large crystals are often formed in this manner. Prolonged agitation with 94.5–97.5% sulfuric acid is a method by which large crystals are sometimes formed; the acid is then diluted to 92% and filtered, when rapid filtration takes place.[27]

The anthraquinone vat dyes give deeply colored vats which vary in color over a wide range. When the alkaline solution is acidified, the leuco compound is characteristically colored, if observed immediately, before turbidity due to separation of sulfur appears. Both indigoid and anthraquinone vat dyes give characteristic colorations in concentrated sulfuric acid and in nitric acid, and utilizing these four color reactions, preferably carried out on the dyed fiber, it is possible to identify many of the commercial vat dyes.[28, 29, 30] The color of some of the dyes in concentrated sulfuric acid undergoes a characteristic change on the addition of a little potassium persulphate,[28] or divanadyl trisulfate,[31] or nitric acid. The dyed fiber, treated successively with acidified permanganate and hydrogen peroxide, undergoes color changes which are useful as supplementary tests, particularly for certain groups of dyes such as the halogenated indanthrones and benzanthrone derivatives.[32] The diluents present in the commercial dyes may affect the color, particularly in sulfuric acid if the dye is examined in substance, and although these diluents are usually water-soluble and therefore readily removable, it is the common and convenient practice to take up the dye on cotton yarn before examination. Herzog's tables include nearly 400 vat dyes, and Bradley and Derrett-Smith have tabulated the properties of 813 vat dyes. Dry-heat tests and observation of the vapors evolved, the indigoids being volatile and the anthraquinonoids generally nonvolatile, and solubility in pyridine and other solvents, are useful for identification.[33] Various other tests which distinguish individual vat dyes have been mentioned:[34] warming with a solution of boric acid in sulfuric acid; adding hydrogen peroxide to a solution in nitric acid; treatment with sulfuric acid and potassium iodate; treatment with alcohol and stannous chloride and observing the fluorescence under an ultraviolet lamp; dissolving in piperidine and observing the fluorescence; and the action of hydrosulfite and caustic soda solution (to which pyridine or piperidine may be added) in stripping the dye from the fiber.

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[27] du Pont, USP 2,180,299.

[28] Herzog, Reactionstabelle der Küpenfarbstoffe, 2nd ed., Wepf, Basle, 1941.

[29] Bradley and Derrett-Smith, *J. Soc. Dyers Colourists* **56**, 97 (1940).

[30] Jones and Kilby, *J. Soc. Dyers Colourists* **41**, 127 (1925).

[31] Mathewson, *Am. Dyestuff Reptr.* **37**, 725 (1948).

Based on his observation that most azoic and indigoid dyes form salts or coordination compounds with alkalis in presence of dry pyridine, Bradley has shown that many anthraquinone intermediates and dyes undergo color changes, giving evidence of the formation of potassium salts or of coordination compounds of potassium salts and pyridine, when a drop of methanolic potassium hydroxide is added to a solution of the anthraquinone derivative in dry pyridine.[35] He has related the character of the color change and the stability of the alkali salt or coordination compound to the constitution of the dye, and especially to the presence of hydroxyl groups and acidic imino groups. Interesting differences are noticed between the behavior of α- and β-aminoanthraquinone, their acyl derivatives, the acyl derivatives of the methylaminoanthraquinones, anthrimides and the corresponding carbazoles, indanthrone and its N-alkyl and halogenated derivatives.

Mixtures of vat dyes are naturally more difficult to identify, and they present problems which have so far been little investigated. Blowing the dyestuff powder on the surface of concentrated sulfuric acid in a porcelain dish is the usual test for detecting the heterogeneity of the dyestuff, as indicated by the appearance of more than one color in the acid; but it is clear that the success of the test depends on the intimacy of the admixture of the constituent dyes, and dyes which have been dispersed together by an efficient technique of standardization will not respond to the test. Color reactions, used in conjunction with the colorations of made-up mixtures of the suspected constituents, provide useful clues, but a definite identification of the individual dyes requires that they should first be separated. Separation may be sometimes effected by fractional precipitation by dilution of the solution in sulfuric acid, depending on differences in the basicities of the dyes. A generally applicable method for the separation of vat dyes is chromatographic adsorption on filter paper or a column of powdered cellulose, using aqueous tetramethylenepentamine containing sodium hydrosulfite for dissolving the dyes and for developing the chromatogram (see also Chapter XLII).[35a]

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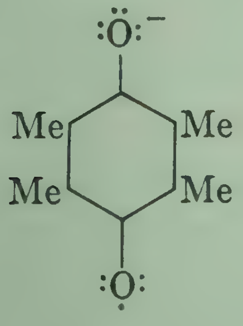
[32] Derrett-Smith and Gee, Society of Dyers and Colourists Symposium on the Theory and Practice of Dyeing, 1947, p. 37.

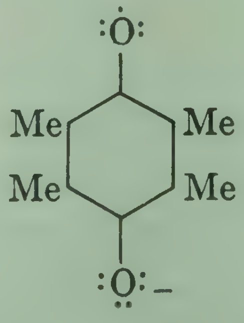
[33] Green and Frank, *J. Soc. Dyers Colourists* **26,** 83 (1910).

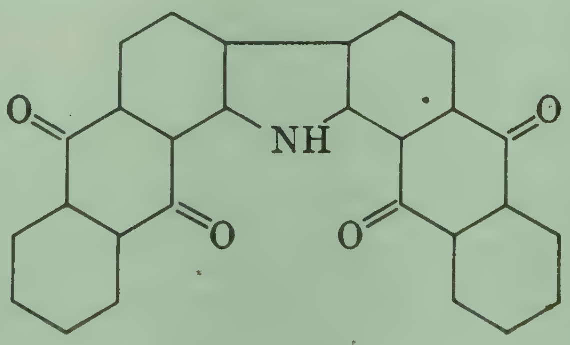
[34] See for example *BIOS* **763.**

[35] Bradley, *J. Soc. Dyers Colourists* **56,** 296 (1940); **57,** 9 (1941); **58,** 2 (1942).

Geake[36] has carried out redox titrations of vat dye systems, and from the curves connecting the potential with the fractional oxidation of the quinol, which is the normal component of the reduced vat, he has produced evidence of the formation of the intermediate semiquinones, especially when titrations are done in presence of pyridine. In the absence of pyridine, semiquinone formation is indicated by color changes, particularly striking with 2,3,7,8-dibenzopyrene-1,6-quinone (Indanthrene Golden Yellow GK) where the quinol is a clear red and the final quinone golden-yellow, but the semiquinone intermediate product is blue. Polarographic studies of anthraquinones have shown that semiquinone formation is often made evident by separate waves or by unusual wave form.[37] The normal redox potentials of unsubstituted carbocyclic quinones are related to the resonance energies of the quinone and the corresponding hydroquinone. Michaelis[38] has shown that the ions of semiquinones, such as (I), the halfway stage in the reduction of duroquinone to duro-


(I)


(II)


Indanthrene Yellow FFRK

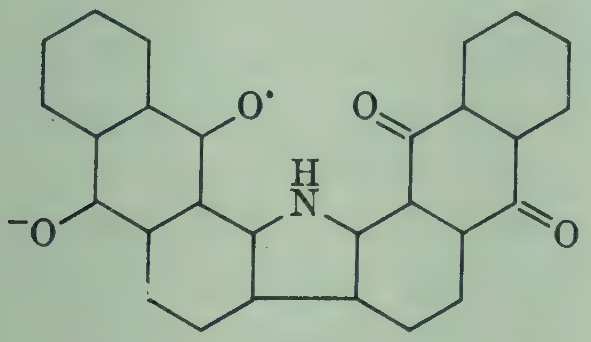
[35a] Rao, Shah, and Venkataraman, *Current Sci.* (*India*), **20,** 66 (1951).

[36] Geake, *Trans. Faraday Soc.* **34,** 1395 (1938); **37,** 68 (1941); Appleton and Geake, *ibid.* **37,** 45, 60 (1941).

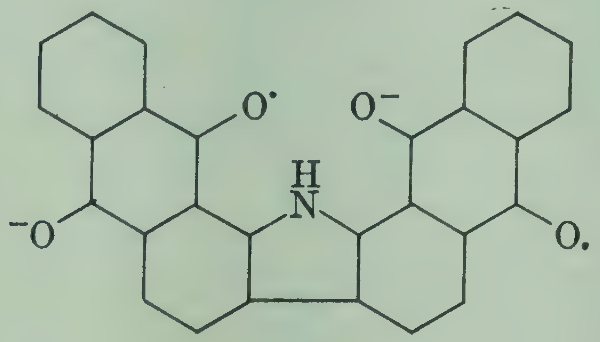
[37] Furman and Stone, *JACS* **70,** 3055 (1948).

[38] Michaelis, *Chem. Revs.* **16,** 243 (1935); Michaelis *et al.*, *JACS* **60,** 1678 (1938).

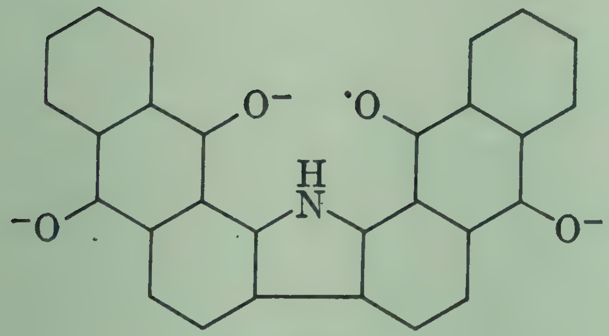
hydroquinone, can exhibit considerable stability. The semiquinones are usually stable only in alkaline solution, the ion being stabilized by resonance between the equivalent structures (I) and (II). When a vat dye containing two anthraquinone systems (e.g. the diphthaloylcarbazole, Indanthrene Yellow FFRK) is vatted, semiquinones will have increased stability, since it is obvious that a structure such as (III) for a semiquinone ion can resonate with three equivalent structures in which the odd electron is on each of the other three oxygen atoms, in addition to resonance with less stable structures in which the unpaired electron is on a carbon atom. Two other types of semiquinones (IV) and (V) can also be formed before the ultimate stage of reduction to the ion (VI) of the tetrahydro derivative is reached. The halfway or dihydro stage of a diquinone should be relatively more stable than the semiquinones (III) and (V), since the ion will be stabilized by resonance between the semiquinone structures, such as IV and VIII, and the quinonehydroquinone structure (VII) in which all the electrons are paired. With indanthrone, discussed later, it is only the dihydro derivative corresponding to (VII) that is formed under normal vatting conditions. The important point that emerges from Geake's work is that semiquinones are also formed



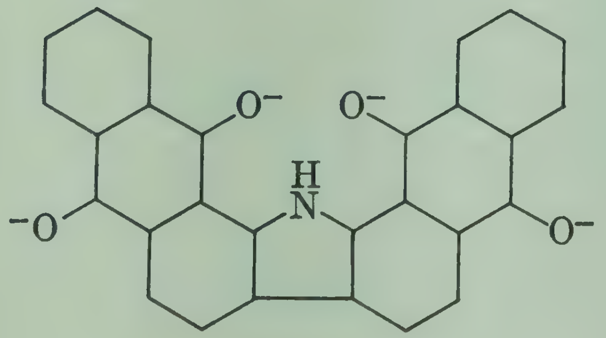
(III)



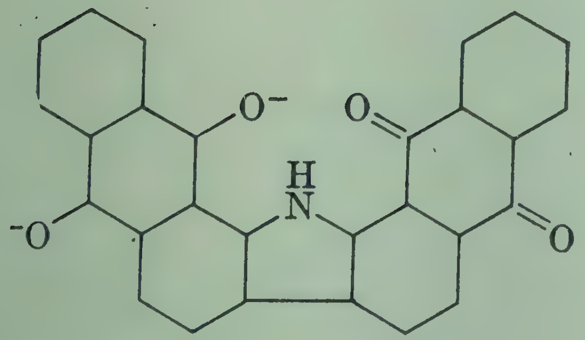
(IV)



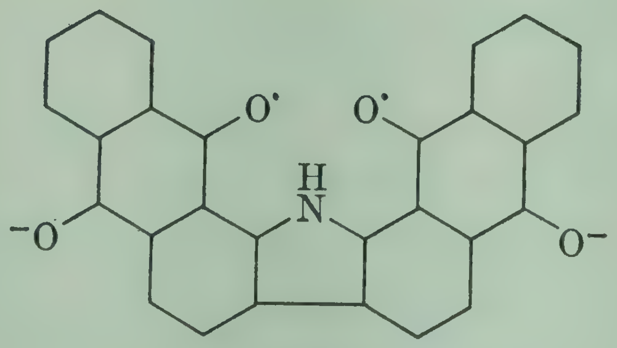
(V)



(VI)



(VII)



(VIII)

when the diquinones are reduced, or when the leuco derivatives are oxidized; both the processes of reduction and reoxidation occur in four stages according as 1, 2, 3, or 4 of the oxygen atoms of the quinone groups are attacked. Geake has further studied the oxidation-reduction behavior of vat dyes in concentrated sulfuric acid, and has suggested that reversible oxidation generally leads to products which are resonance hybrids of structures in which two electrons have been lost by various pairs of carbon atoms.

Application of Anthraquinone Vat Dyes

The anthraquinone vat dyes are applied to cotton and other cellulose fibers from a hydrosulfite-caustic soda vat.[38a] Depending on the quantities of these reagents and the temperature of vatting and dyeing, different processes are distinguished; further, the addition of common salt or Glauber salt is necessary for dyes which have relatively low substantivity for the fiber and do not exhaust well. Thus IG classified the main dyeing methods as IN, IW and IK (Indanthrene Normal, Warm and Kalt) processes (Table I), in accordance with variations in the caustic

TABLE I

<table>
<tr><th><i>Process</i></th><th><i>IN</i></th><th><i>IW</i></th><th><i>IK</i></th></tr>
<tr><td>Caustic soda solution 70° Tw (32.5%), pints per 100 gals.</td><td>8–13</td><td>3.25–6.5</td><td>2.5–5</td></tr>
<tr><td rowspan="6">Hydrosulfite lbs. per 100 gals.</td><td colspan="3">For dyeings using</td></tr>
<tr><td colspan="2">a) 1–2.5% dyestuff</td><td>1–2 lbs.</td></tr>
<tr><td colspan="2">b) 2.5–5% ,,</td><td>2–2½ lbs.</td></tr>
<tr><td colspan="2">c) 5–10% ,,</td><td>2½–3 lbs.</td></tr>
<tr><td colspan="2">d) 10–20% ,,</td><td>3–4 lbs.</td></tr>
<tr><td colspan="2">e) more than 20% dyestuff</td><td>4–6 lbs.</td></tr>
<tr><td>Common salt lbs. per 100 gals.</td><td>None</td><td>a) 5
b) 10
c) 15
d) 20
e) 25</td><td>50% more than for IW process</td></tr>
<tr><td>Temperature of dyeing</td><td>50–60°</td><td>45–50°</td><td>18–25°</td></tr>
<tr><td>Time of dyeing in minutes</td><td>20–45</td><td>30–60</td><td>30–60</td></tr>
</table>

[38a] A committee of the Society of Dyers and Colourists has recently reported on the dyeing properties of vat dyes and has described migration and strike-leveling tests (see Chapter XLII) for determining level-dyeing properties; *J. Soc. Dyers Colourists* **66,** 505 (1950).

soda and salt additions and in the time and temperature of dyeing.[39] A simpler grouping is into strong alkali and weak alkali dyes, and indeed the alkali concentration is perhaps the most significant factor in view of its effect on the protein fibers and its influence on the rate of absorption of the vatted dye.[39a]

The percentages of dyestuffs in Table I are the weight of dyestuff pastes of normal concentration for 100 lbs. of yarn. Table I refers to dyeing yarn in an open beck in which the length of liquor is 1 to 20; and for machine dyeing, in which this is usually 1 to 10, the quantities of caustic soda and hydrosulfite have to be increased by about 50%. Cloth is usually dyed on the jigger; larger amounts of hydrosulfite and caustic soda are necessary than for yarn dyeing, because of the repeated exposure of the impregnated material to air.[39b] The classification and the figures in Table I are general indications, and the conditions actually used have to be varied in accordance with requirements. Paste brands are vatted directly, but powder brands may have to be pasted with Turkey Red oil or other wetting and emulsifying agents before reduction. The reduction of the dyestuff may be carried out in the total volume of water to be used as dyebath; a more convenient procedure, especially for certain dyes, is to prepare a concentrated or "stock vat," and add this in two portions to the dyebath which is previously "sharpened" or deoxygenated by the addition of a little hydrosulfite and caustic soda. The presence of an adequate excess of hydrosulfite and caustic soda, in the absence of which the insoluble parent dye will precipitate, is tested for from time to time. Some of the anthraquinone vats (e.g., several of the violets, greens, and the IN type in general), having very high substantivity, are apt to be absorbed by the fiber too rapidly and to give unlevel shades; the dyeing process has then to be controlled by such devices as adding the stock vat in several portions, increasing the length of the liquor, lowering the temperature of dyeing and adding retarding agents (e.g., glue, sulfite cellulose liquor, or special products recommended by dye manufacturers). Careful control of the dyeing process by these methods is especially necessary for pale shades. After impregnation, the leuco compound is oxidized to the insoluble dye by lifting the yarn, wringing and allowing to oxidize in the air. In machine dyeing, oxidation may be accelerated by treatment with a solution containing 0.05% potassium dichromate and 0.1–0.2% sulfuric acid, or with a 0.2–0.3% solution of sodium perborate. The dyed material is then washed, soured in dilute acid, washed, and finally soaped at the boil with 0.2% soap solution for 30 minutes. For dyes which are known to tender cellulose on exposure to light,[40] the soaped material must be thoroughly rinsed since alkalinity favors the degradative action.

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[39] See also Müller, *Melliand Textilber.* **28**, 93, 136, 273 (1947).

[39a] Fox, *J. Soc. Dyers Colourists* **65**, 508 (1949), has recently reviewed the dyeing and fastness properties of the anthraquinonoid vat dyes in relation to their constitution. He has also discussed the tendency of the vats to over-reduction, hydrolysis, dehalogenation and molecular rearrangements.

[39b] A novel continuous dyeing process is to pass cloth successively through the dye liquor and a molten metal at 95–105°; excess of dye liquor is thus squeezed out and uniform penetration is obtained; Boardman, *J. Soc. Dyers Colourists* **66**, 397 (1950).

X-Ray diagrams of cellulose dyed with a series of vat dyes have shown that they can be classified into three groups according as they remain amorphous, crystallize by aftertreatment with boiling soap solution, or simply by oxidation.[41] Only indigo has been identified as belonging to the last group. Indanthrone belongs to the first group, remaining amorphous even after soaping; most anthraquinonoid vat dyes belong to the second group, being amorphous on the fiber after adsorption and oxidation, but forming crystallites on aftertreatment.[42] An example is Indanthrene Brilliant Scarlet RK; the shade on cellulose is strongly shifted from yellow to red by aftertreatment, and the X-ray diagram reveals that the color change results from the crystallization of the dye, which can be effected by merely soaking in cold water for several hours.

In dyeing compound shades it is preferable to mix dyes which belong to the same dyeing class, but this is by no means a rigid rule, since the classification merely indicates that the best results are generally obtainable under the given conditions and a dye normally suitable for one process may well be applied by an alternative process.

A wide range of shades is available in the anthraquinone vat dye series. In brightness most of them are somewhat inferior to the indigoids and considerably inferior to the azoics, but mellow shades are preferable for many purposes. The anthraquinonoids are rich in blues, greens, browns, khakis, and blacks. There are useful scarlets and reds, but in comparison with the azoics the tinctorial power is low and relatively large quantities of the dyes are necessary to produce full shades. A serious defect of many of the yellow and orange vat dyes of the anthraquinone series is their property of accelerating the degradative action of light and bleaching agents (e.g. hypochlorite) on cellulose.[40] Such dyes are therefore unsuitable for curtains and other materials that are liable to be exposed to light for long periods. During the oxidation of the leuco derivative to the vat dye on the fiber, by means of air or other oxidizing agents, severe degradation of the cellulose can occur. This is mainly true of the photochemically active vat dyes, but under the optimum conditions of pH and redox potentials, any anthraquinonoid vat dye can exhibit this unpleasant property, so that the oxidation stage of the vat dyeing process has to be handled with care if an oxidizing agent other than atmospheric oxygen is employed. Tendering can also occur when fabrics containing yarn dyed with yellow and orange dyes are bleached with hypochlorite or hydrogen peroxide. However, research is leading to a continual extension of the vat dye range to fill in the gaps in the color scale and to include dyes which are free from the defects of the older members of the series.

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[40] See Chapter XL.

[41] Valko, *JACS* **63,** 1433 (1941).

[42] See also Bean and Rowe, *J. Soc. Dyers Colourists* **45,** 67 (1929).

For cellulose fabrics which have to meet high fastness requirements, the anthraquinone vat dyes are the dyes of choice. The average fastness to light of the dyes in the commercial range is 7; fastness to washing and to chlorine 4–5; and fastness to soda boil 3–4. Mixtures of dyes must be carefully chosen since the fastness (e.g., to light) is sometimes lower than that of any of the component dyes. The anthraquinonoids are particularly suitable for dyeing yarn which is to be woven into fabrics and bleached in the piece, although precautions are necessary during kier boiling to prevent marking off or bleeding of the dye by the combined action of hot alkali and the reducing agents which may be present in (or be formed from) the size and other materials in the cloth. Thus sodium carbonate in a concentration of about 0.5 to 1% and a temperature of 55–60° are employed, and an oxidizing agent, such as sodium *m*-nitrobenzenesulfonate, may be added.

Many vat dyes tend to change in shade by hot pressing and by water spotting. The change is reversible, and the original shade usually returns. Some of the dibenzanthrones and isodibenzanthrones for instance become redder or yellower when the dyed material is wetted, but on drying the true shade is restored. Vigorous soaping of the dyed material, which removes surface color and assists the crystallization of the dye within the fiber, diminishes the effect of water spotting and hot pressing. The color changes of some vat and azoic shades by water spotting and by wet and dry heat have been variously attributed to hydration and dehydration, changes in the state of aggregation of the pigment, and oxidation.[43]

Pigment padding process. For closely woven cotton fabrics made up from highly twisted yarns and for linen, presenting difficulties in penetration, the "pigment padding process" is conveniently employed. The fabric, thoroughly scoured, is impregnated in a padding machine with an aqueous dispersion of the unreduced vat dye; the dispersion is prepared from a paste or powder fine brand of dyestuff with the aid of

[43] See also Kornreich, *J. Soc. Dyers Colourists* **62,** 318 (1946); **58,** 177 (1942).

wetting and protective colloidal agents such as highly sulfated and sulfonated oils.[43a] The padded cloth is then treated in a jigger, or a continuous developing machine,[44] with hydrosulfite and caustic soda solution, rinsed with cold water, treated with perborate solution to complete the oxidation of the vat, and finally soaped. The pigment padding process is being increasingly used for a wider variety of fabrics than the drills and duck cloths for which it was originally developed. In the du Pont "pad-steam-continuous dyeing process" the pigment-padded fabric is dried in a hot-air flue, padded with a solution of hydrosulfite and caustic soda below 38° (common salt and sodium formaldehydesulfoxylate being added to prevent the migration of the dye into the liquor and to continue the reduction after the exhaustion of the hydrosulfite), and passed through a steaming chamber at about 101° from which air is excluded.[45] During this passage, which is of very brief duration (under a minute), reduction to the leuco compound and its immediate penetration into the fiber swollen by the action of steam take place uniformly. Oxidation and soaping are then carried out as usual. For dyeing union fabrics of cotton and viscose, ICI suggest the addition of gum tragasol (a locust-bean gum which is coagulated by alkali) to the pigment padding liquor; the function of the gum is to prevent the dye from bleeding into the reducing bath and redyeing the rayon preferentially.

Vat acid process. A recent and important IG development is the vat acid process, in which the vat dye is reduced as usual by means of hydrosulfite and caustic soda, but at high concentration, and the leuco solution is acidified with acetic acid in presence of a dispersing agent such as Setamol WS or an Igepon or Dispersol AC.[46–48] The leuco derivative or vat acid, which is thus formed in a highly dispersed condition, is then applied to yarns and fabrics by the stock vat dyeing or padding process; further treatments are as in the pigment padding process. In fact, the basic idea in the pigment padding and vat acid methods is similar. Like the unreduced insoluble dye, and unlike the soluble alkali salt of the vat acid, the vat acid itself has practically no affinity for cellulose, and this lack of substantivity is a great advantage for many purposes, such as the dyeing of viscose in filament or staple fiber form and of cotton-viscose unions. Impregnation takes place in a homogeneous manner since it is effected mechanically, and level dyeing is then achieved by solubilization of the dye within the fiber walls and subsequent oxidation. The vat acid process, which is applicable to many but not all vat dyes, has been reported on favorably by a Committee of the AATCC.[49]

[43a] For a study of solvation in relation to the stability of vat dye suspensions and their migration, see Graham and Benning, *J. Phys. & Colloid Chem.* **53,** 846 (1949).

[44] Williams, *Am. Dyestuff Reptr.* **36,** 256 (1947). See also Womble, USP 2,396,908.

[45] Newman, *Am. Dyestuff Reptr.* **34,** 99 (1945); Vieira and du Pont, USP 2,415,379; Stott and Shimp, USP 2,487,197.

[46] *BIOS* Misc. **20.**

[47] *FIAT* **644;** *BIOS* **1773.**

[48] Hennessey, *Am. Dyestuff Reptr.* **36,** 775 (1947); Mueller, *ibid.* **39,** 113 (1950); Marney and ICI, BP 634,973.

Viscose and cellulose acetate. While the anthraquinone vat dyes are as suitable for dyeing viscose as for cotton, their application to viscose calls for the usual precautions necessary for this fiber. The alkali salts of the leuco derivatives are first adsorbed, almost instantaneously, and there is a second and distinct stage of relatively slow diffusion into the interior of the fiber.[50] The ability of a vat dye to give level shades, which depends on the rates of exhaustion and diffusion, has to be studied in terms, for instance, of the "strike test."[50,51] The principle of the test is to introduce two skeins of yarn or squares of fabric successively into a dyebath at a time interval of 10 seconds or one minute, and estimate the time taken for obtaining the same shade on the two specimens. The cold dyeing (IK) process is unsuitable for viscose. The strong alkali dyes are dyed at 35° to 60°, the temperature being raised slowly; and many weak alkali dyes give good results by dyeing at temperatures up to 80°.

Union fabrics of cotton or viscose and cellulose acetate can be dyed with vat colors, adding β-naphthol to the dyebath to prevent saponification of the acetate; under these conditions the cellulose acetate is undyed and can be dyed subsequently by means of a dispersed dye. It is also possible to dye acetate rayon with the vat dyes themselves by methods which are modifications of the pigment padding process. Thus it may be dyed by impregnating with a vat dye dispersion, reducing to the leuco compound by hydrosulfite and sodium carbonate, and oxidizing.[52] The precipitates obtained by adding ethanol to aqueous solutions of leuco vat dyes are suitable for dyeing cellulose acetate.[53]

Viscose cake may be dyed by an application of the pigment padding principle.[54] An aqueous dispersion of the unreduced dye is circulated through the cake, and the deposition of the dye on and in the fiber is effected by the gradual addition of common salt. The dye is then reduced by circulating hydrosulfite-caustic soda solution. As oxidizing agent sodium hypochlorite is satisfactory for weak shades, but other conventional methods may be used. This process may also be applied to cotton in package form.[55]

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[49] Gilchrist, *Am. Dyestuff Reptr.* **36,** 142 (1947).

[50] Boulton and Morton, *J. Soc. Dyers Colourists* **55,** 481 (1939).

[51] Burgess, *J. Soc. Dyers Colourists* **62,** 41 (1946).

[52] British Celanese, BP 578,212.

[53] British Celanese, BP 592,778.

[54] Cox, *J. Soc. Dyers Colourists* **62,** 44 (1946); Abbott, Cox and ICI, BP 593,008.

Calico printing. For a considerable time the anthraquinone vat dyes were difficult to apply in calico printing; because of slow reduction and poor penetration during ageing, weak specky prints were apt to be produced. These problems have now been largely overcome by a careful study of the behavior of each dye at various stages of the printing process and selection of suitable dyes. The physical state of the dye plays an important part in printing, and dye manufacturers market special printing brands (e.g. Suprafix dyes, IG). Besides efficient dispersion, ready vatting may be facilitated by the addition of reduction catalysts, such as anthraquinone and hydroxyanthraquinones. The main process for calico printing is to make up the printing paste with a thickening of dextrin or British gum, glycerine, potassium carbonate, sodium formaldehyde-sulfoxylate and a substance such as sodium *N*-benzylsulfanilate which improves the solubility and gives clearer prints. After printing, the fabric is dried and aged for a few minutes in a Rapid Ager or Festoon Ager. Oxidation is effected by passage through a dichromate solution, and the material is finally soaped at the boil. In the pre-reduction process, which shortens the ageing time, but has the disadvantage that the printing paste has poor keeping qualities and must be used immediately after preparation, the dyestuff paste, thickened with British gum and glycerine, is mixed with potassium carbonate (or caustic soda, the alkalinity of which is later reduced by the addition of bicarbonate), and hydrosulfite. The mixture is heated at about 50° until reduction is complete, cooled, mixed with sodium formaldehyde-sulfoxylate, made up to the required volume by more thickening, and printed. In the Colloresin process, recommended for screen printing and for printed materials which have to be stored for a time before steaming, the thickening agent is Colloresin DK (IG), partially methylated cellulose which is soluble in cold water, but insoluble in boiling water and in cold or hot aqueous alkali; as a result, the printed fabric has no tendency to bleed or mark off during the subsequent padding in alkali-hydrosulfite solution and wet steaming. A popular British process is to print the cloth with paste containing unreduced vat dye and locust-bean gum thickening, dry and pad in a liquor containing alkali and sodium formaldehyde-sulfoxylate, dry and age as usual.

The presence of a single quinone system appears to promote printing quality; vat dyes which print well also make good leuco sulfuric esters.[55a]

[55] Richardson and Wiltshire, *J. Soc. Dyers Colourists* **63,** 224 (1947).

[55a] Barrick, *Am. Dyestuff Reptr.* **39,** 324 (1950).

Since the alkaline reducing agent present in the vat dye printing paste will decompose an azoic dye, vat dyes are valuable for producing colored discharges on azoic grounds.

Reserve effects under a vat dyed or printed ground may be produced by destroying the reducing agent which is necessary for vatting and subsequent fixation to take place, and by preventing any reduced vat dye from penetrating the fabric. A reagent suitable for this purpose is *m*-nitrobenzenesulfonic acid (a mild oxidizing agent) in conjunction with manganese and zinc salts which form a membrane of the hydroxides by interaction with alkali. A mechanical method of resisting the leuco compound is to print a design on a fabric by means of water-repellent waxes or resins, prior to dyeing; this is used in the old art of "battick dyeing."

The stability of the anthraquinone vat dyes to oxidizing agents and the marked substantivity of the leuco compounds to cellulose render the discharge style of printing difficult for vat dyed grounds. However, reasonably good results can be obtained with a limited number of vat dyes by using a discharge paste containing formaldehyde-sulfoxylate, caustic soda, zinc oxide and a quaternary ammonium salt of the type of Leucotrope W (IG) (Metabol WS, ICI). By an ageing treatment at about 102°, addition of sodium silicate (water-glass) to the soaping bath, and a final bleach with hypochlorite, clear whites can be produced.

Stripping vat dyes. The removal of a vat dye is obviously difficult, but satisfactory stripping has now become possible by the introduction of special products which restrain the reabsorption of the leuco compound by the fiber. The method consists in boiling the dyed fiber with hydrosulfite and caustic soda solution together with a stripping auxiliary, such as Peregal O (IG) (Dispersol VL, ICI) which is a fatty alcohol-ethylene oxide condensate, Albatex PO (Cb) which is a benzimidazole sulfonate, Leucotrope W (IG) which is phenylbenzyldimethylammonium chloride, or Lissolamine V (ICI) which is a quaternary ammonium salt of the type of cetylpyridinium (or trimethylcetylammonium) bromide.

Wool, silk and nylon. The indigoid and thioindigoid vat dyes are usually preferred to the anthraquinone vat dyes for application to wool and silk, but the protein fibers can be dyed with the anthraquinone vat dyes by suitably controlling the alkalinity of the dyebath and the temperature of dyeing. Dyes of the IK type requiring relatively low concentrations of alkali for vatting and dyeing are chosen. Vatting is carried out with the minimum amount of caustic soda, and for any additional alkali required in making up the bath soda ash, ammonia or trisodium phosphate is used. The milder alkalis, especially trisodium phosphate, may completely replace caustic soda for selected dyes.

Ammonium sulfate or chloride is employed for exhausting the dye liquor, the salts serving the additional purpose of controlling the pH.

Nylon is remarkable in its behavior towards vat dyes. The affinity of the vats is generally poor, and the light fastness of the shades, which have excellent fastness on cotton, is nearly as low as that of the basic dyes. No really satisfactory explanation of these phenomena has been advanced so far.[56] The fastness to light of dyeings or prints produced with vat dyes or leuco ester salts on nylon is considerably improved by steaming them for about 40 minutes at 3 atmospheres pressure, after developing and soaping as usual.[57] Aftertreatment with phenols or phenolic acids, which do not have a swelling action on the fiber, increases the light fastness of vat dyes on nylon.[57a]

Nontextile uses. The fastness of the vat dyes to alkali renders them suitable for coloring paper pulp (e.g., for soap wrapping papers and printed wall papers), washable distempers and cement.[58] Paper pulp may be dyed by methods similar to the dyeing of cotton.[59] Considering their high light fastness and great stability, anthraquinonoid vat dyes are of interest as pigments, but their use is limited by the cost, and by the relatively low covering power of many of the dyes. They are useful for instance in coloring plastics (including rubber), since they withstand the temperatures used in moulding and the chemicals used in vulcanization.[60] Vat dyes manufactured primarily for dyeing and printing textiles, as well as vat dyes made specially for use as pigments, are employed in the coloration of paints, varnishes, lacquers, enamels and like materials. For use as pigments vat dyes have to be produced in special physical forms with the maximum covering power or color value, miscibility with vehicles and extenders, absence of bronzing, and other desirable properties. Vat dyes may be used for producing photographic prints on textiles by padding them successively with a dispersion of a vat dye and a solution of ferric ammonium citrate. When the dried cloth is exposed to light under a negative, the ferric salt is reduced to the ferrous salt in the exposed portions. The ferrous salt vats the dye, so that dyeing takes place and, on oxidation, a positive colored print results.[61]

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[56] Cf. Rose, *Am. Dyestuff Reptr.* **31,** 204 (1942).

[57] Durand and Huguenin, BP 603,154.

[57a] Butterworth and Crosland, BP 632,083.

[58] Forster, Kudva and Venkataraman, *J. Indian Chem. Soc., Ind. Ed.* **6,** 119 (1943).

[59] Lips, *Paper Trade J.* **118,** No. 13, 31 (1944).

[60] See Black, *Ind. Eng. Chem.* **32,** 1304 (1940).

[61] Bleachers Association, BP 597,982.

CHAPTER XXXI

ANTHRAQUINONE VAT DYES—ANTHRAQUINONE DERIVATIVES

ACYLAMIDOANTHRAQUINONES

Among the anthraquinone vat dyes, the acylamidoanthraquinones are notable for their simplicity of structure and of the method of preparation. The aminoanthraquinones are capable of vatting, but the alkali salts of the leuco compounds have no affinity for cotton, and Deinet (1909) observed that benzoylation of 1-aminoanthraquinones had the remarkable effect of transforming them into vat dyes with adequate affinity for practical dyeing. It is an important fact that one or more of the acylamido groups must be in the α-position of the anthraquinone nucleus; while α-benzamidoanthraquinone is a yellow vat dye (Algol Yellow WG) (By; CI 1126), the β-isomer is devoid of dyeing property.[1] Di-β-anthraquinonylurea was once marketed as Helindone Yellow 3GN (Schmidt and Kränzlein, 1909) (MLB; CI 1138) (Algol Yellow 4GK; ST 1250), but is now obsolete. A mixed α- and β-acylamidoanthraquinone derivative, obtained by condensing β-aminoanthraquinone with an equimolecular proportion of phosgene to form the carbamyl chloride and then condensing two moles of the latter with one mole of a mixture of 1,5- and 1,8-diaminoanthraquinone, was at one time marketed as Helindone Brown 3GN (Schmidt and Kränzlein, 1909) (MLB; CI 1148). Aliphatic monocarboxylic acids are inadequate for imparting the necessary intensity of color and substantivity, but two moles of an aminoanthraquinone, preferably a monobenzoyl diamine, may be linked together by means of phosgene or an aliphatic dicarboxylic acid. Algol Yellow WG is no longer employed commercially in view of its moderate fastness to light (4) and its relatively low tinctorial power. The technically valuable dyes are derivatives of the diamino and triaminoanthraquinones, or of 1-aminoanthraquinone condensed with an aromatic dicarboxylic acid. However, one benzamido group is sufficient for more complex anthraquinone derivatives, such as the pyrimidanthrones. Further, the introduction of a benzamido group is a simple and convenient method for modifying the shades and improving the dyeing properties of other types of anthraquinone vat dyes.

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[1] See Chapter XLI.

The shades of the acylamidoanthraquinones are yellow, orange, red and violet; they do not include blues, greens and blacks. The reds in this group have low tinctorial power, and several of the yellows and oranges are active tenderers.[1a] The dyes are mainly applied by the cold or IK method for the reason that the optimum results are obtained under these conditions; there is little danger of hydrolysis of the acylamido groups under hot dyeing conditions, as sometimes suggested. The dyes dissolve in alkaline hydrosulfite at 20–25°, using a relatively small amount of caustic soda, and the addition of salt is necessary for exhausting the bath. The color of the vats is generally pale red, red-brown or red-violet, and the color of these dyes in sulfuric acid is pale yellow, orange or red-brown. The levelling properties are good. The fastness to wet treatments and to chlorine is generally as high as among other anthraquinone vat dyes, the exceptions being the violet dyes which contain hydroxyl groups. The light fastness of most of the yellow dyes in the series is low (4–5) in comparison with the excellent light fastness of the anthraquinone vat dyes as a class, but the reds and violets reach the latter standard.

Preparation. The usual technical method of preparation[2–4a] is to treat the amine with the acid chloride in boiling nitrobenzene or *o*-dichlorobenzene for a few hours. On cooling, the dye is collected and washed with the solvent. Most of the acylamidoanthraquinones can be readily prepared by this simple procedure, but various modifications have been suggested in the patent literature. Acid-binding agents such as fused sodium acetate may be used. The acid chloride may be prepared *in situ* by using the acid and phosphorus pentachloride, and anthraquinonylamides of aliphatic dibasic acids have been prepared in this manner. Heating the aminoanthraquinone with an ester or amide of the acid has been suggested;[5] when α-aminoanthraquinone is heated with ethyl oxalate, the product is a red dye which probably has the structure AQ—N=C(OEt)—C(OEt)=N—AQ, in which AQ is α-anthraquinonyl.[6] Another method is to condense a halogenated anthraquinone with an acid amide in presence of a copper catalyst and sodium acetate;[7] pure α-benzamidoanthraquinone is obtained by heating α-chloroanthraquinone with benzamide in presence of potassium carbonate and copper bromide in an amount equal to the weight of chloroanthraquinone.[8] High molecular vat dyes, which contain amino groups and are sparingly soluble in organic solvents, can be benzoylated by agitating with benzoyl chloride at about 100°, and adding a little concentrated sulfuric acid. By acylating the leuco compound of an aminoanthraquinone in nitrobenzene solution, oxidation to the dye may be simultaneously effected.[9] Leuco-1-amino-4-acylamidoanthraquinones have been prepared by treating stable leuco-1,4-diaminoanthraquinone with acid halides under conditions which prevent oxidation to the keto form, e.g., by condensing in *o*-dichlorobenzene and pyridine mixture at 25°; by subsequent heating in nitrobenzene at 130° oxidation to the anthraquinone takes place.[10] The preparation of pure monoacyl derivatives directly from the diaminoanthraquinones has to be done under specific conditions.[11] For partial benzoylation 1,5-diaminoanthraquinone is heated in nitrobenzene at 150–155° for three hours with benzoyl chloride (1.6 moles) and sodium carbonate, when 1-amino-5-benzamidoanthraquinone (I) and 1,5-dibenzamidoanthraquinone are formed in a proportion of 3:2. On cooling to 120° and filtering, the more soluble monoacyl derivative is recovered from the filtrate.[12] 1-Amino-4-benzamidoanthraquinone (II) has been prepared[12] in 90% yield by heating leuco-1,4-diaminoanthraquinone with nitrobenzene and a little piperidine at 150°, cooling to 15° and agitating

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[1a] See Chapter XL.

[2–4a] IG methods are described in *BIOS* (2) **987**; (3) **1493**; (4) *Misc. Report* **20**; and (4a) *FIAT* **1313** II.

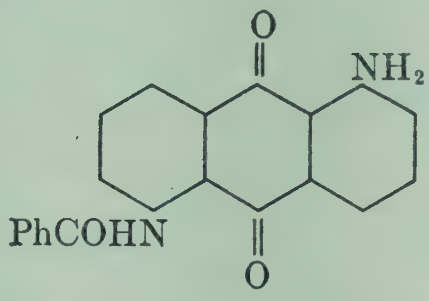
[5] IG, DRP 210,019; 212,436; 216,980.

[6] IG, DRP 270,579; see also Billimoria, IP 31,437.

[7] Bayer, DRP 216,772; Ciba, SP 251,645; 257,292.

[8] Buxbaum and du Pont, USP 2,346,726.

(I)



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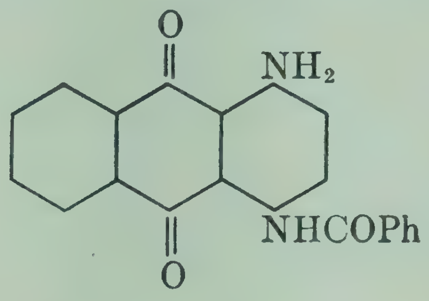

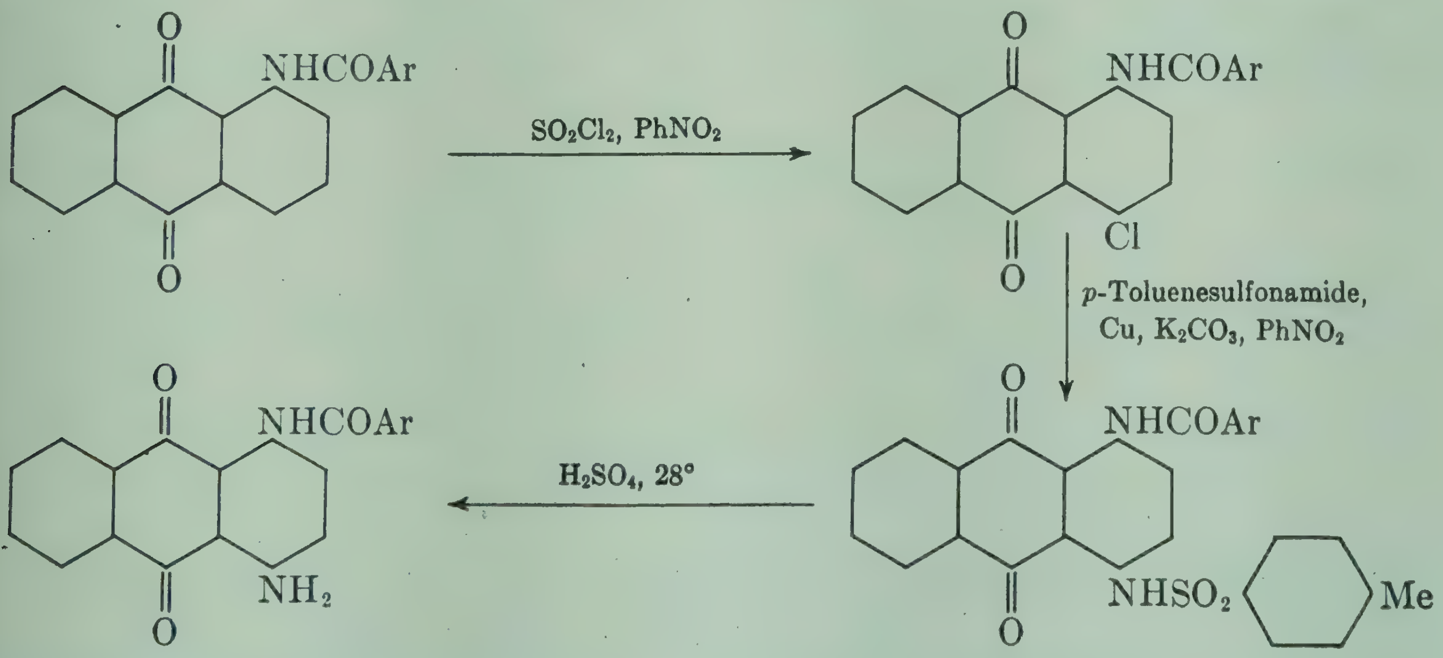

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[9] British Dyestuffs, Shepherdson, Tatum, and Banbury, DRP 484,357.

[10] du Pont, BP 571,154.

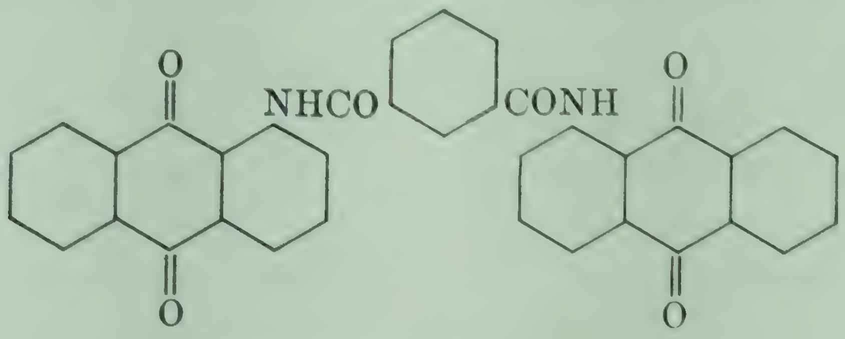
[11] IG, DRP 462,053; 522,787; BP 276,692.

[12] *BIOS* **1484.**

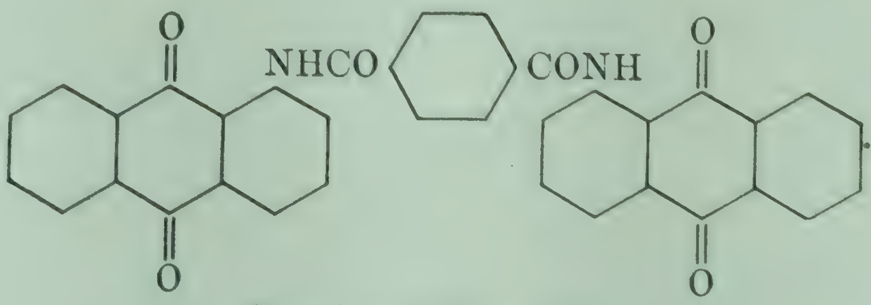
with benzoyl chloride (2 moles) and sodium carbonate solution. The mixture is filtered and the filter-cake freed from unreacted diamine by treatment with hydrochloric acid. Monoaroyl derivatives of diamines have also been prepared from the diaroyl derivatives by partial hydrolysis with oleum;[13] and from 1-aroylamidoanthraquinones by the indicated series of reactions.[14]

Constitution and shades. The general method for determining the constitution of the acylamidoanthraquinones is hydrolytic fission by means of sulfuric acid[15] or 20% alcoholic potassium hydroxide,[16] followed by identification of the amine and acid components.

While 1-benzamidoanthraquinone is obsolete, 1-salicylamidoanthraquinone (Helio Fast Yellow 6GL) (By; CI 1127) has a limited use as a pigment. The condensation product of α-aminoanthraquinone and diphenyl-4-carboxylic acid (Indanthrene Yellow BY 1609) was made by IG for use in the manufacture of the solubilized vat dye, Anthrasol or Indigosol Yellow V.[3] By condensing two moles of α-aminoanthraquinone with succinic acid, the product is Algol Yellow 3G (Fischer, 1908) (By; CI 1139), which is obsolete; but replacing the aliphatic acid by isophthalic acid and terephthalic acid, two useful dyes are obtained: Indanthrene Yellow 5GK (ST Erg. II 1217a)[17] and Paradone Yellow



Indanthrene Yellow 5GK



Paradone Yellow 5GK

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[13] Il'inskii and Zaikin, *Anilinokras. Prom.* **2,** No. 10, 24 (1932).

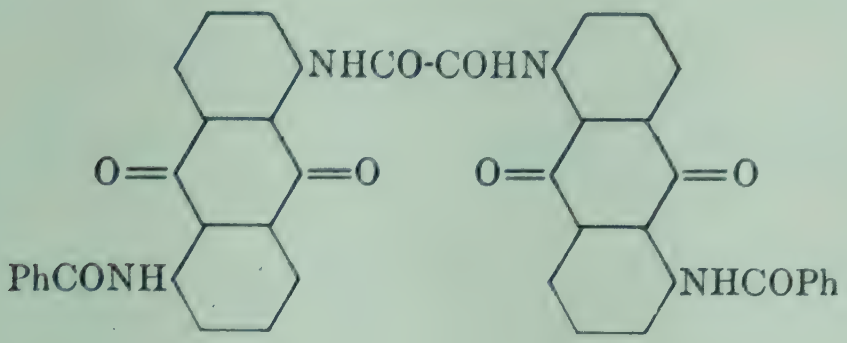
[14] Cf. Loveluck, Thomas, and ICI, BP 375,848.

[15] Il'inskii and Zaikin, *J. Gen. Chem.* (*U.S.S.R.*). **4,** 1294 (1934).

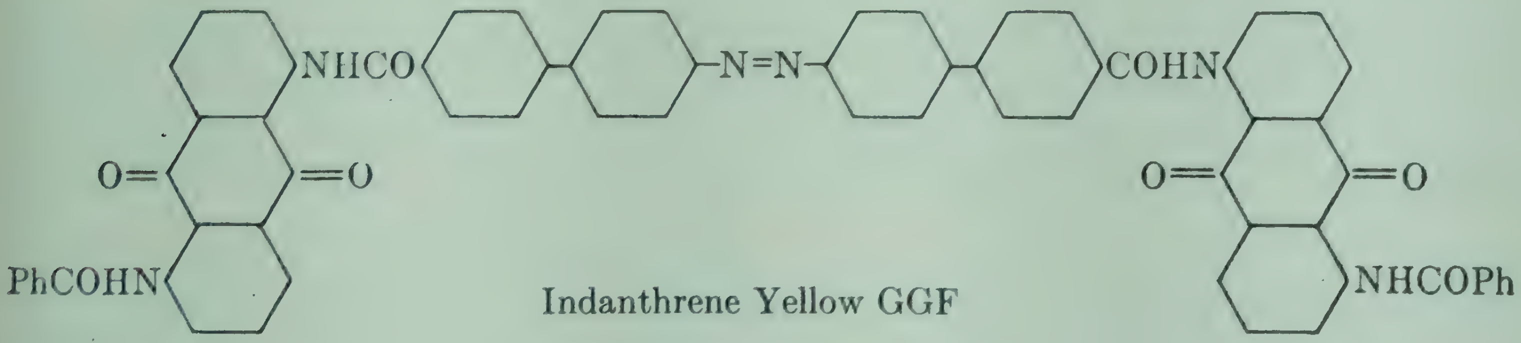
[16] Sunthankar and Venkataraman, *Proc. Indian Acad. Sci.* **25A,** 467 (1947); **32A,** 240 (1950).

[17] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935.

5 GK (LBII);[18] these are important as the only pure yellow dyes among the acylamidoanthraquinones, the other yellows being red in tone.[18a] 1,5-Bisbenzamidoanthraquinone (Noelting and Wortmann, 1906; CI 1132) (Algol Yellow R; Indanthrene Yellow GK; Caledon Yellow 3G) is little used at the present time. Indanthrene Yellow 3GF (ST Erg. II 1217b)[3] which dyes a reddish yellow from a gray-green vat is interesting as using both an aromatic and an aliphatic acid for acylation. It is prepared by condensing (I) with oxalyl chloride.[19] The commercial dye is a little redder than the pure compound of authentic structure, owing to the presence of the 1,8-isomer.[20] Condensing two moles of (I) with one of terephthalic acid, the product is Caledon Yellow 4G, stated to be a nontenderer.[1a] Another interesting derivative of (I) obtained by condensation of two moles with one of 4-azodiphenyl-4′,4″-dicarboxylic acid (prepared by the reduction of 4-nitrodiphenyl-4′-carboxylic acid with glucose and caustic soda) is Indanthrene Yellow GGF;[2] its light fastness (6–7) in full shades is better than that of the other yellow acylamidoanthraquinones, but the dye is little used because of the high cost. A notable feature of Indanthrene Yellow GGF is the stability of the azo group, which is unaffected by hydrosulfite and alkali at 60°.



Indanthrene Yellow 3GF



Indanthrene Yellow GGF

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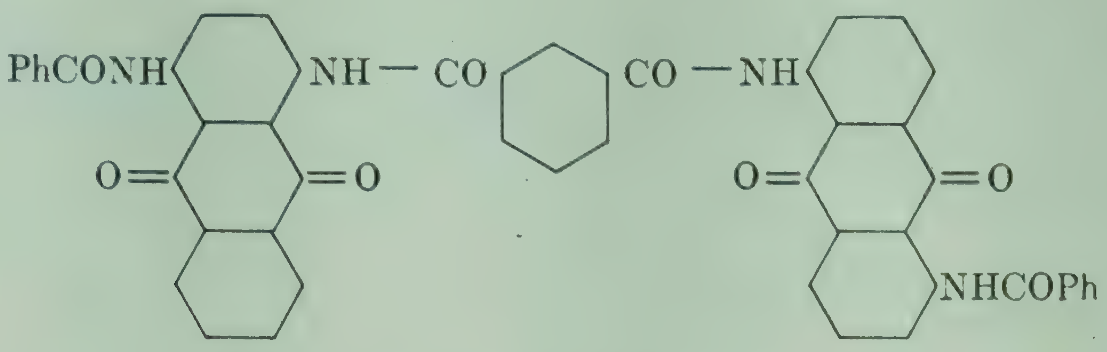
[18] Fraser-Thomson in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. I, Longmans, London, p. 402.

[18a] The introduction of *N*,*N*-dimethylsulfonamide groups in the 6,6′-positions in Paradone Yellow 5GK gives a dye which dyes cotton a pure and fast yellow shade; Ciba, SP 260,308.

[19] IG, DRP 448,286.

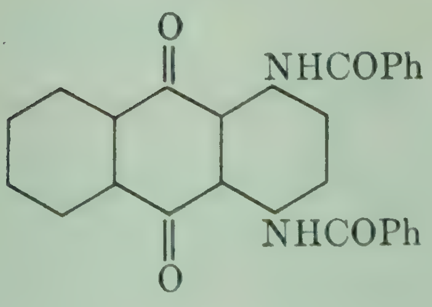
[20] Hefti, *Helv. Chim. Acta* **14**, 1404 (1931).

Indanthrene Orange GG, a derivative of both 1,5- and 1,4-diaminoanthraquinone, has excellent all-round fastness (light 7–8, soda-boil 4–5, chlorine 5) and it is a nontenderer; it is prepared by condensing isophthalic acid with one mole each of (I) and (II).[63]

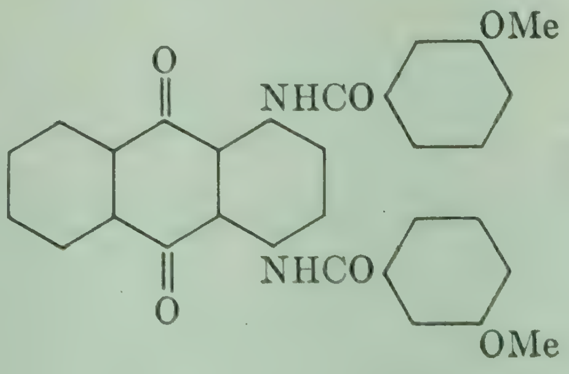


Indanthrene Orange GG

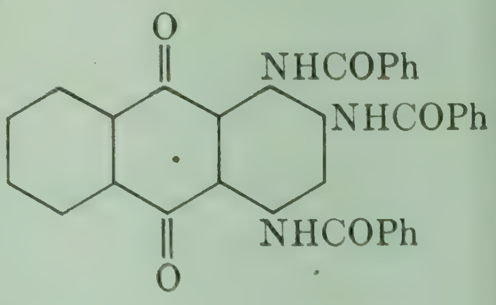
1,4-Bisbenzamidoanthraquinone is the important dye, Indanthrene Red 5GK (Deinet, 1909; CI 1131) (Caledon Red 5G), which has excellent light fastness (7–8) and very good fastness to chlorine (4). After studying the products of the condensation of numerous acid chlorides with the usual aminoanthraquinones, IG found that *m*-substituted benzoyl chlorides, especially *m*-methoxybenzoyl chloride, isophthaloyl chloride and trimesic acid chloride, gave valuable dyes in respect of shade and fastness.[2] Indanthrene Red BK is the *m*-methoxybenzoyl analog of Red 5GK. The *p*-aminobenzoyl analog of Indanthrene Red 5GK has been mentioned as Indanthrene Brown G (ST 1219), but it is doubtful if this diamine was ever marketed. The later brand of Brown G consisted of a mixture of Indanthrene Brown R (CI 1151) and Olive R or 3G. By the addition of a benzamido group in the 2-position in Indanthrene Red 5GK, a hypsochromic effect is produced in Indanthrene Orange RRK (CI 1136) (Algol Brilliant Orange FR).[21] Indanthrene Orange RRK is prepared by nitrating and reducing 1,4-bisbenzamido-



Indanthrene Red 5GK



Indanthrene Red BK



Indanthrene Orange RRK

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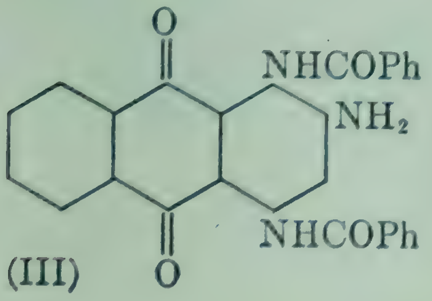
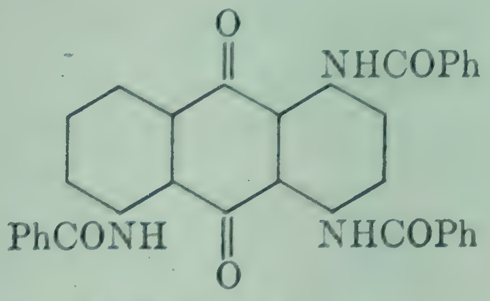
[21] In Ref. 18 Indanthrene Orange RRK has been formulated as an imidazole derivative.

anthraquinone to the 2-amino compound (III), which is then benzoylated; (III) is also of interest as the intermediate from which the imidazole derivative, Indanthrene Orange FFRK, is prepared. When a third benzamido group is introduced in 1,4-bisbenzamidoanthraquinone in the 5-position, the shade is altered towards a considerably bluer red (Algol Bordeaux 2B; Caledon Red X5B).[18] A bright red dye of exceptional fastness is made by at least 80% mononitration of 1,4-bisphthalimidoanthraquinone, hydrolyzing the *N*-phthaloyl groups, reducing the nitro group, and benzoylating.[22] The dyes (IV) give brilliant bordeaux shades of "remarkable fastness to light and wet treatments."[23]

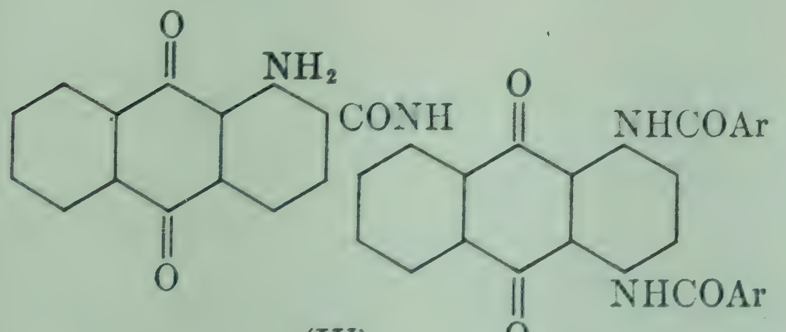


(III)



Caledon Red X5B

The introduction of hydroxyl and methoxyl groups in the anthraquinone nucleus of 1-benzamidoanthraquinone has a marked bathochromic effect; the 4-hydroxy compound is Algol Pink R (By; CI 1128), which is also used as a pigment (Helio Fast Pink RL); the 4-methoxy compound is Algol Scarlet G (By; CI 1129), and the 4,5,8-trihydroxy compound is Algol Violet B (By; CI 1130). The introduction of a hydroxyl group in the 4-position in Indanthrene Yellow GK gives a red dye, Algol Brilliant Red 2B (By, CI 1133) (Algol Pink BBK; Caledon Red FF). The introduction of a further hydroxyl group in the 8-position gives a violet dye; the shade and fastness properties are improved by replacing benzoic acid by anisic acid. Two important dyes are obtained in this manner; Indanthrene Brilliant Violet RK (Thomaschewski, 1908) (By; CI 1135) is the dianisoyl derivative of 4,8-diaminoanthrarufin, while



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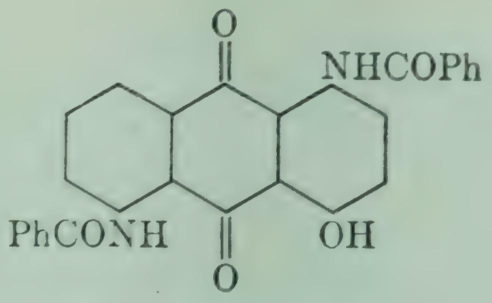

Algol Pink BBK

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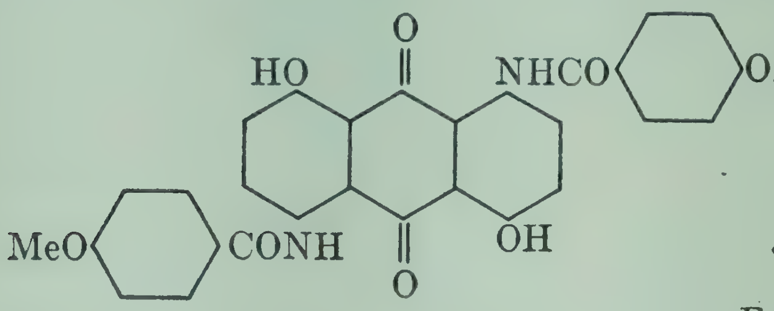
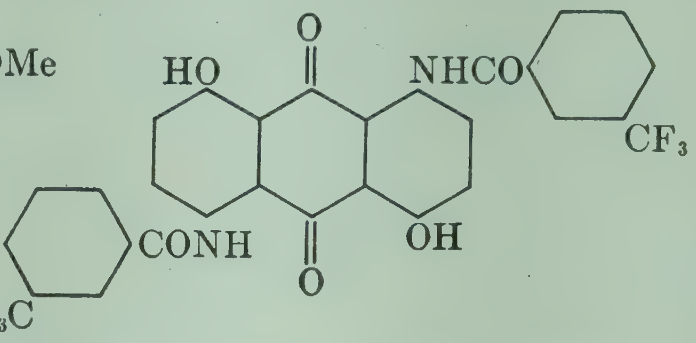
[22] ICI, BP 365,565.

[23] Irving, Livingston, and ICI, USP 2,447,981.

Indanthrene Brilliant Violet BBK[3] is a mixed dye in which this diamine (1 mole) is condensed with anisoyl chloride (1.25 mole) and benzoyl chloride (1.12 mole). Their fastness to washing and chlorine (3–4) is below the standard of other anthraquinone vat dyes, but they have excellent fastness to light (7 and 7–8); the hydroxyl groups are responsible for the lower fastness to alkali. Brilliant Violet F3RK is a recent IG introduction, stated to be specially useful for dyeing cotton-viscose unions and to have better wash fastness than Violet RK.[24] 1,4,5-Trisbenzamido-8-hydroxyanthraquinone, containing only one hydroxyl group, has been claimed to be a fast blue dye.[25]

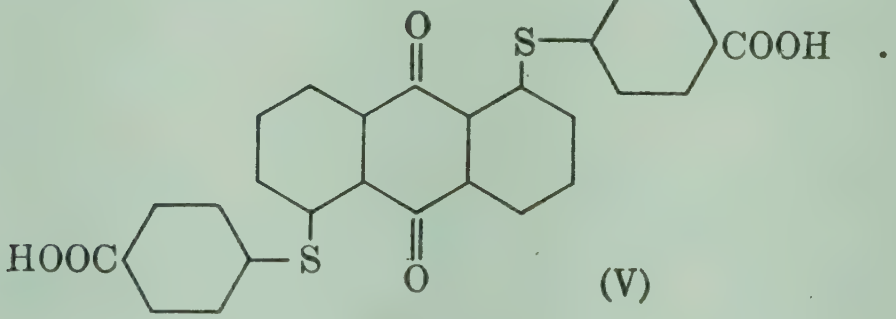


Indanthrene Brilliant Violet RK



Indanthrene Brilliant Violet F3RK

In addition to the acids employed for the dyes already introduced into commerce, many hundreds have been suggested in patents. The products obtained by acylating 1-aminoanthraquinone with *o*- or *p*-cresotinic acid dye wool from a weakly alkaline vat in greenish yellow shades of great fastness.[26] 1,5-Bis-*p*-chlorobenzamidoanthraquinone gives strong and fast shades when applied at 40–50°.[27] Naphthalene-2,6- and 2,7-dicarboxylic acids give bright yellow-red and red-brown shades of very good fastness. Dibasic acids, such as diphenylmethanedicarboxylic acid, diphenyl-*p*,*p*′-dicarboxylic acid, and their halogen substituted derivatives, have been condensed with α-aminoanthraquinone and its substitution products to give fast yellow, orange and red shades.[28] Fluoranthenedicarboxylic acid condensed with (I) gives a yellow dye.[29]



(V)

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[24] *FIAT* **1313** III.

[25] Ciba, BP 459,770.

[26] IG, BP 442,949.

[27] Sutter, Kern, and Ciba, USP 2,420,453; Ciba, BP 604,916.

[28] IG, BP 339,267; DRP 562,916.

[29] Ciba, SP 219,414. See also SP 224,880–7.

Yellow to orange dyes have been synthesized by condensing aminoanthraquinones with diphenyl ether 4,4′-dicarboxylic acid, diphenyl disulfide dicarboxylic acid, and acids such as (V).[30] These dyes, especially phthaloyldiphenyl sulfide derivatives, are claimed to have excellent fastness properties. Bright scarlet to red vat dyes of good fastness, particularly to kier boiling, are obtained by the introduction of two different alkane- or phenylalkanesulfonylbenzoyl groups into 1,4-diaminoanthraquinone.[31] The acyl residues may contain sulfonamide groups.[31a] Vat dyes of the anthrimide, carbazole and other types have improved printing properties when they contain benzamido groups, the benzene ring carrying an alkyl or aryl sulfoxide or sulfone substituent.[32] 2-Hydroxy-3-naphthoic acid derivatives are of interest, as they are vat colors capable of coupling with diazonium salts.[33] Thus (VI) dyes a bright lemon-yellow as a vat dye, and the shade on the fiber can be modified by after-treatment with diazonium salts. Anthraquinonoylamidoanthraquinones form a distinct group, in which both the components are derived from anthraquinone, resulting in easy vatting and probably in increased affinity for cellulose, but no dye of this type appears to have been marketed. The condensates of 2-chloroanthraquinone-6-carboxylic acid and aminoanthraquinones give orange to red dyes of high tinctorial power and fastness, and dyes containing a third anthraquinone residue may be obtained by condensation with an α-aminoanthraquinone, so that the dyes belong also to the anthrimide class.[34] A pure red vat dye has been prepared by the action of ammonia on the condensate of α-aminoanthraquinone and 1-chloroanthraquinone-2-carboxychloride.[35] Red to violet dyes are obtained by treating a 4,8-diamino-1-aroylamidoanthraquinone with 2 moles of 1-nitro-, amino-, or chloroanthraquinone-2-carboxylic acid.[35a] The range has been extended by condensing 1-aminoanthraquinone-2-carboxylic acid and its functional derivatives with 1-amino-4-, 5-, or 8-arylaminoanthraquinones to get deep and fast corinth shades.[36] Red to red-brown dyes have been made by condensing 1-amino-4-benzamidoanthraquinone or 1,4-diaminoanthraquinone with 1,4-bisaroylamidoanthraquinone-6-carboxylic acid.[37] Olive, brown, gray and black-green dyes are produced by condensing 1-benzamido-4-*p*-carboxyanilinoanthraquinones or their derivatives, capable of use as vat dyes, with vattable primary aminoanthraquinones or their derivatives;[38] an example is (VII)[39] which is an olive dye. A series of vat dyes have been described which are prepared from anthraquinone-2,6-dicarboxylic acid by condensation with two moles of a vattable amine.[40] An unusual intermediate is 1-amino-3-benzoylanthraquinone, which yields with terephthaloyl chloride a greenish yellow and with cyanuric chloride a reddish yellow dye.[41]

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[30] IG, DRP 566,169.

[31] Irving, Livingston, and ICI, BP 568,933; see also Ciba USP 2,439,626; BP 605,701; SP 239,953; 242,510–1.

[31a] Ciba, BP 605,466; 635,924; 636,691; see also SP 252,533; 257,942–51.

[32] Ciba, BP 580,642.

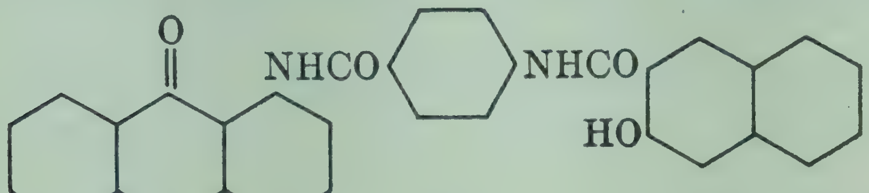
[33] Bhat, Gavankar, and Venkataraman, *J. Indian Chem. Soc. Ind. Ed.*, **5**, 171 (1942); see also Jusa and Riesz, *Monatsh.* **58**, 137 (1931).

[34] Deinet and du Pont, USP 2,181,048.

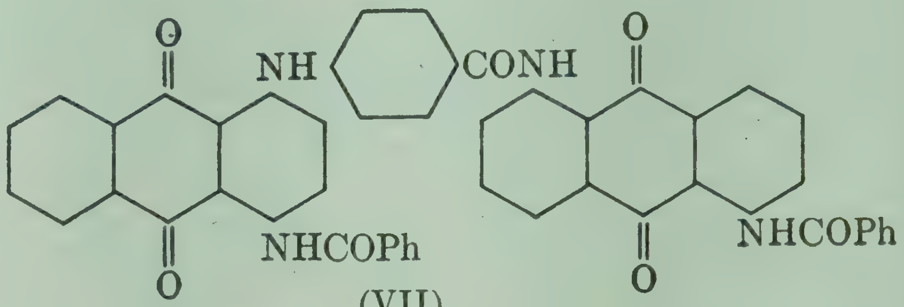
[35] Rollett, *Monatsh.* **46**, 131 (1925).

[35a] Livingston and ICI, BP 631,213.

[36] IG and Honold, DRP 648,770. See also Ciba, SP 253,257; 258,772–5; 261,068.

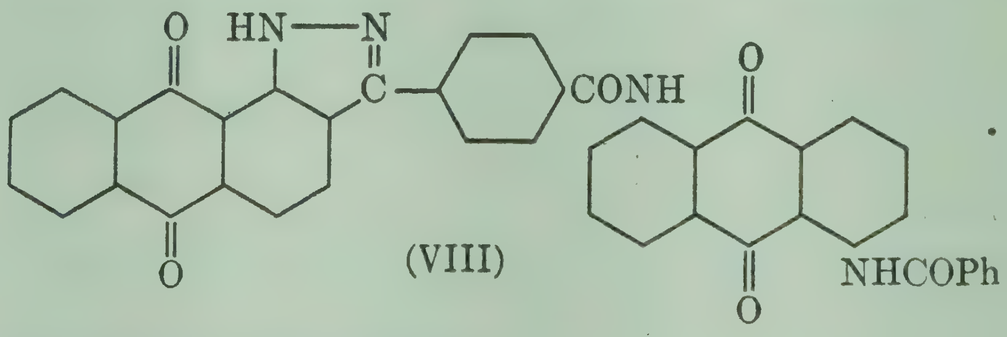


(VI)



(VII)

Carboxylic acids derived from heterocyclic compounds, which may themselves be nonvattable or vattable, are the subject of numerous patents. Furoyl derivatives[42] give weak yellow to yellow-brown shades, but the nitrogen- and sulfur-containing heterocyclic acids augment the tinctorial power considerably. The condensation products of benzothiazole-2-carboxylic acid, quinolinecarboxylic acids,[43] diphenylene oxide dicarboxylic acids, and *N*-ethylcarbazole dicarboxylic acids have been mentioned.[44] A yellow dye with very high fastness properties, applicable by the IN process, is (VIII); its high cost has precluded its commercial



(VIII)

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[37] Graham and du Pont, USP 2,179,552.

[38] Sandoz, BP 561,420.

[39] Peter and Sandoz, USP 2,374,891.

[40] Ciba, BP 585,874. See also SP 247,603–612; 259,729; USP 2,459,941.

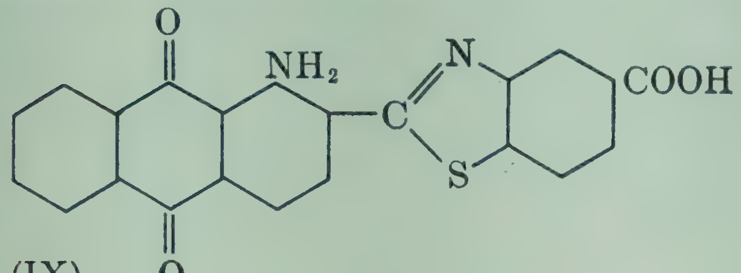
[41] Ciba, BP 517,434.

[42] Wilder, *J. Colo. Wyo. Acad. Sci.* **1,** No. 3, 23 (1931).

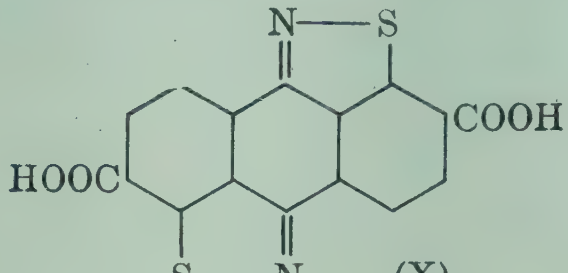
[43] IG, DRP 602,336; 606,461; 579,325.

[44] Honold and IG, DRP 555,182.

exploitation.[2] Anthraquinonyl benzothiazole carboxylic acids such as (IX) yield pleasant bordeaux dyes,[45] and bright yellow dyes are obtained by condensing 1,9-thiophenanthrone-3-carboxylic acid with α-aminoanthraquinone or monobenzoyl diaminoanthraquinones.[46] Ciba have investigated the complex compounds obtained by acylating any vattable amino compound with a nonvattable heterocyclic dicarboxylic acid. The preparation of derivatives of thianthrene, thioxanthone, phenoxthine and dibenzo-*p*-dioxin have been described, the vattable residues being anthraquinone, dibenzanthrone, pyranthrone, etc.[47] Red to violet dyes have been prepared by acylating aminoanthraquinones or their derivatives with 1-amino-4- or -5-carboxyanilino-1-(*N*)-9-anthrapyridones.[48] Red to orange vat dyes of very good fastness have been prepared by condensing a heterocyclic acid like 1,9,5,10-anthradiisothiazole-3,8-dicarboxylic acid (X) with aminoanthraquinones.[49]



(IX)



(X)

Cyanuric Acid Derivatives

Dyes in which two or three aminoazo compounds are linked together by condensation with cyanuric chloride have been described in Chapter XVI. Similar condensation of aminoanthraquinones with cyanuric chloride serves the more fundamental purpose of providing a new mode of acylation which converts an aminoanthraquinone into a vat dye.[50] While the cyanuration of the soluble azo dyes is carried out in aqueous solution, the aminoanthraquinones are condensed in a suitable organic solvent. Nitrobenzene was suggested in earlier patents, cuprous chloride being sometimes used as a catalyst, but phenol is a much better solvent for cyanuration of the aminoanthraquinones. Fierz-David and Matter[51] have prepared the secondary compound (I), which dyes shades similar to those of Cibanone Yellow 2GR and Indanthrene Yellow 3GF, but they were unable to effect the condensation of a third aminoanthraquinone molecule, using nitrobenzene or tetralin as solvent, together with cuprous chloride. The tertiary compound is obtained smoothly in excellent yield in boiling phenol;[52] an IG patent[53] refers to aromatic hydroxy compounds in general and states that the preferred temperature is 80–150°. With α-aminoanthraquinone itself, both the yellow dyes produced by the condensation of two or three moles with one of cyanuric chloride are valueless, since they are powerful tenderers.[54, 1a] Commercial representatives are Cibanone Orange 6R, Red G and Red 4B. Cibanone Red 4B is the tertiary condensation product of cyanuric chloride with 1-amino-4-benzamidoanthraquinone.[55] Cibanone Orange 6R is the analog of Red 4B with methoxyl groups in place of the benzamido groups. 1,4-

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[45] IG, Zerweck, and Honold, DRP 618,811; 619,403.

[46] Stilmar and du Pont, USP 2,233,496.

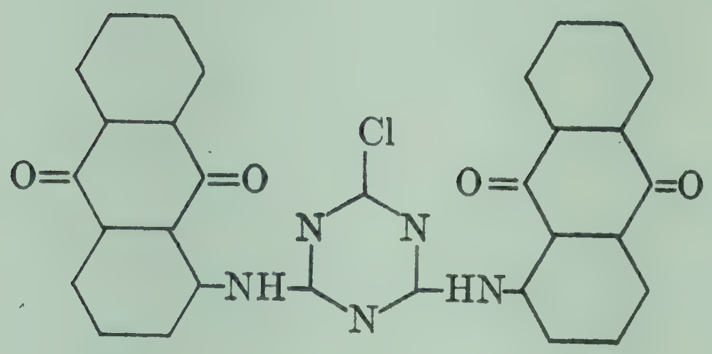
[47] Ciba, BP 555,055; SP 236,231; 238,627–36; 240,129; 243,008.

[48] Sandoz, BP 560,131.

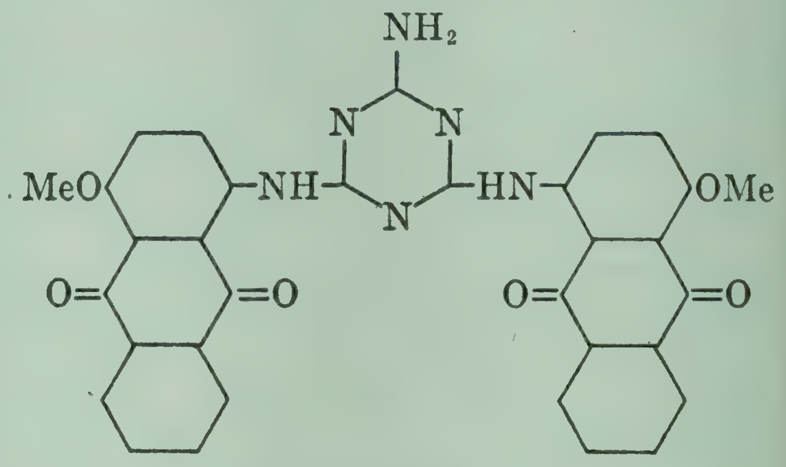
[49] Ciba, BP 580,681; Holbro, Kern, Suter and Ciba, USP 2,408,259. See also SP 244,838.

[50] Ciba, SP 97,059; 100,397–401; 101,405; 104,011–4; 104,713; 108,210–16; 108,856–7; 112,533–7; 114,834; 116,076–7; DRP 390,201; 399,485; BP 205,525; 223,911; 231,688; 234,086; 237,872; IG, DRP 590,163; IG, BP 350,575.

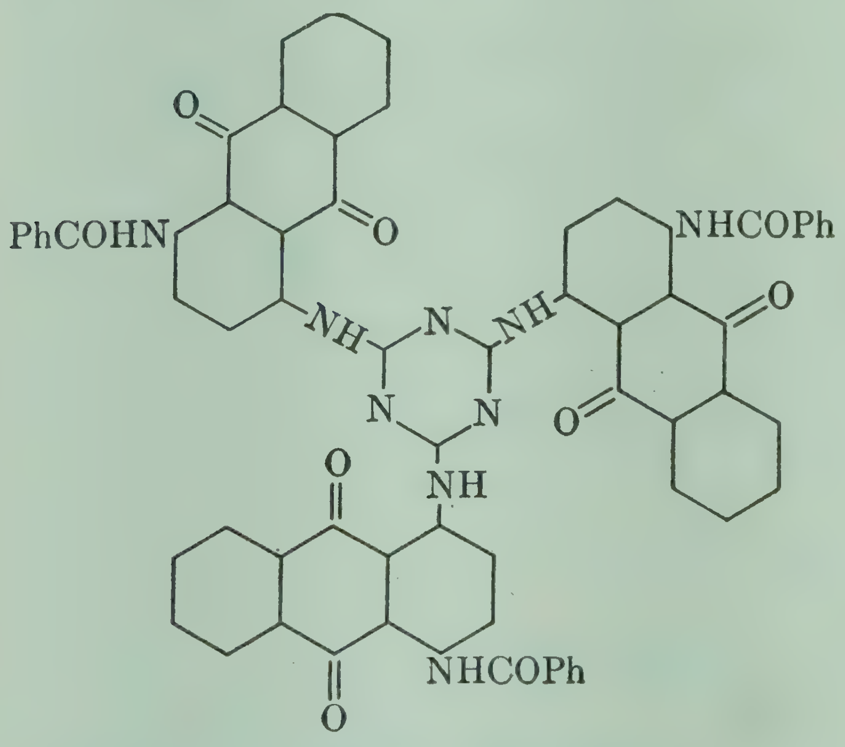
[51] *J. Soc. Dyers Colourists* **53,** 434 (1937).



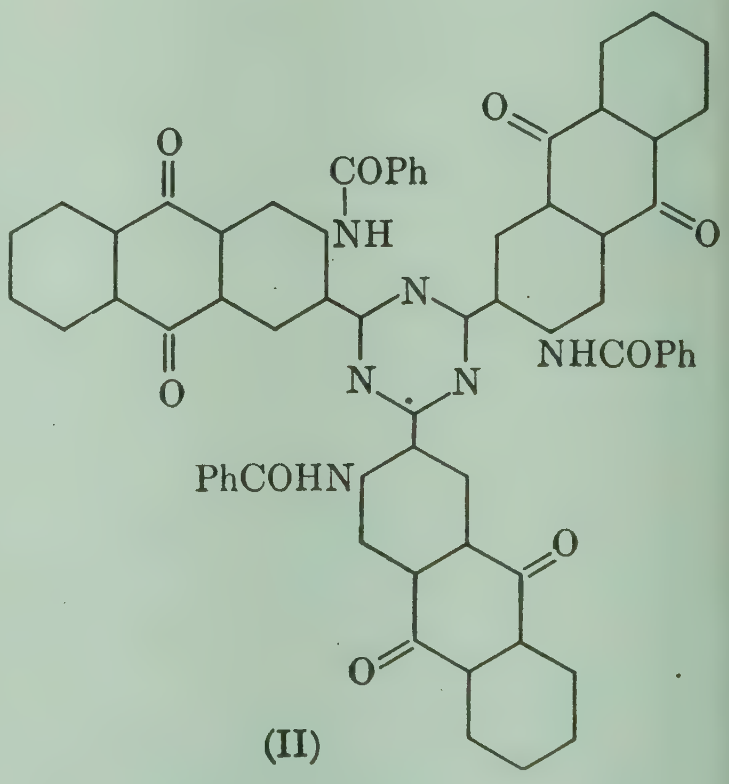
(I)



Cibanone Red G



Cibanone Red 4B



(II)

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[52] Talavadekar, unpublished work.

[53] DRP 375,056.

[54] See, however, Lecher, Eberhart, and American Cyanamid, USP 2,479,943.

[55] Jayaraman, unpublished work.

Diaminoanthraquinone on cyanuration gives a red-violet dye, and if the reaction is effected in presence of copper a pure red dye.[18, 50] Cyanuration of 5-amino-1,4-bisbenzamidoanthraquinone gives a bluish red dye of great brilliance and tinctorial power.[55a]

A procedure for the preparation of vat dyes in which the aminoanthraquinone and triazine residue are linked together by a C–C bond is to polymerize a nitrile; thus 2-benzamido-3-cyanoanthraquinone gives the orange dye (II).[18]

ANTHRIMIDES

The simplest "anthrimides" are the dianthraquinonylamines (AQ-NH-AQ), prepared by the condensation of a chloroanthraquinone with an aminoanthraquinone under the usual conditions of the Ullmann reaction; of the three isomers (1,1′; 2,2′; and 1,2′), it is only the last or mixed type which behaves as a vat dye (Isler, 1905) marketed under the name of Algol Orange R (Indanthrene Orange 6RTK; CI 1137); the dye is now obsolete. More useful dyes are obtained by introducing benzamido groups, and by increasing the number of anthraquinone residues to form trianthrimides. While the technically useful dyes are mostly the mixed α,β-types, the α,α′-compounds are important as intermediates for the preparation of anthraquinonecarbazoles, among which are some of the fastest dyes in the entire range of anthraquinone vat colors. Further, the introduction of an anthraquinonylamino group is a method of modifying the shade of anthraquinone vat dyes of other types. The anthrimides dye somewhat dull shades of orange, red, bordeaux, and gray, which have excellent all-round fastness (light 6–8; other agencies 4–5). The orange dyes are tenderers.[1a] They are mostly applied by the IK process; their substanstivity and tinctorial power are generally poor.

Preparation. The main method is the interaction of the appropriate chloro compounds and amines in boiling nitrobenzene in presence of sodium carbonate and copper bronze. Other acid-binding agents (e.g. fused sodium acetate) and copper salts (copper chloride or sulfate) may be added, and in special cases molten naphthalene or other solvents may be employed in place of nitrobenzene. The time of heating varies from a few hours to as long as 48 hours, depending on the complexity of the anthrimide. The orientation of the amino group and the halogen atom has an important effect on the formation of the anthrimides. If both are in the α-position the reaction takes place easily, e.g., α-chloroanthraquinone reacts readily with α-aminoanthraquinone to form 1,1′-dianthrimide. If one group is in the β-position the reaction takes place with rather more difficulty, and it is advisable to condense the β-halogen compound with the α-amine. When both the halogen atom and the amino group are in the β-position the reaction takes place with difficulty, and for obtaining good yields an iodo compound is preferably employed.[56]

[55a] Irving, Livingston, and ICI, BP 602,975.

A typical procedure is illustrated for a pentanthrimide. 1,4,5,8-Tetrachloroanthraquinone (80 kg.), α-aminoanthraquinone (206 kg.), soda ash (60 kg.) and copper powder (2.7 kg.) are charged to a copper pan containing nitrobenzene (1890 kg.), and the mixture vigorously agitated for 36 hours at 205°. The reaction is complete when the residue from an alcohol extract of a test sample, previously washed with excess ligroin, gives only a slight color to a solution of boric acid and acetic anhydride. The product is purified by extracting with alcohol, and distilling off the solvent.[3]

After carrying out the reaction in boiling nitrobenzene or molten naphthalene, a useful method of purification of some anthrimides is to filter the hot solution, which removes the unreacted components. In view of the toxicity of nitrobenzene and the inflammability of naphthalene at high temperatures, the nitrobenzene or naphthalene solution is blown from the reaction kettle to the filter-press by means of nitrogen, and the filter-press is enclosed and exhausted in order to avoid inhalation of nitrobenzene vapors by the workers and the danger of cyanosis. A method of preparation not involving the use of solvents is to heat the chloro compound (e.g. 1-benzamido-5-chloroanthraquinone) and the amine (e.g. 1-aminoanthraquinone), together with sodium carbonate and cuprous chloride, in a rotary baker (ball or rod mill) at 200–220° for several hours until the evolution of water and carbon dioxide ceases; a yield of 84–86% of the anthrimide is obtained.[57]

Among other methods for the preparation of anthrimides may be mentioned the condensation of aminoanthraquinones with nitroanthraquinones in a solvent such as *o*-dichlorobenzene in presence of anhydrous potassium carbonate.[58] Anthrimides are also formed by heating aminoanthraquinones with sodium anthraquinone sulfonates.[59] A novel method for the preparation of β,β′-dianthrimide is to treat anthraquinonediazonium chloride with ammonia, and heat the product with a solvent of high b.p. with or without a condensing agent.[60] The general reaction of the addition of a primary amine to a quinoneimide may be used for the preparation of 4,4′-diamino-1,1′-dianthrimide and its derivatives. While two moles of aniline can be reacted together in presence of an acid to form diphenylamine, an α-amino- and a β-aminoanthraquinone can be condensed in presence of sodium carbonate and copper oxide to form an anthrimide.

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[56] Eckert and Steiner, *Monatsh.* **35,** 1129 (1914).

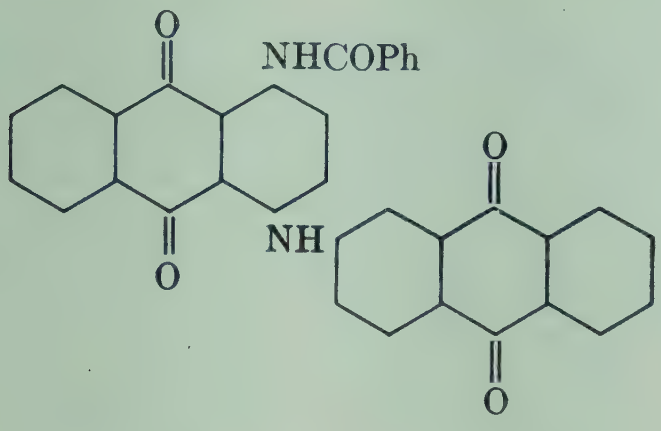
[57] Tinker, Stallmann, and du Pont USP 2,420,022; BP 603,495–6.

[58] MLB, DRP 201,327.

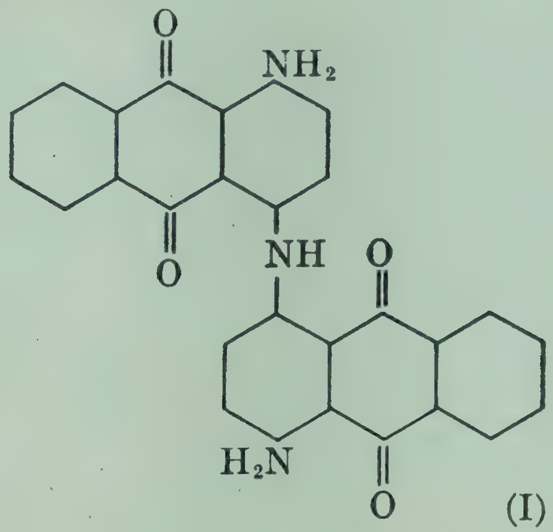
[59] MLB, DRP 216,083.

[60] MLB, DRP 308,666.

Constitution and shades. The simplest anthrimide which is a useful dye is Indanthrene Corinth RK (Algol Corinth R), prepared by the condensation of 1-amino-4-benzamidoanthraquinone with 2-chloroanthraquinone (contrast CI 1144) in naphthalene solution at 205° (8 hours) in the presence of sodium acetate and carbonate, copper powder and copper acetate.[3] A red-brown dye is obtained by condensing 2-chloroanthraquinone with the anilide of 1-aminoanthraquinone-6-carboxylic acid.[61] Condensation of 2-chloroanthraquinone-6-carboxyl chloride with 6-chloro-1-aminoanthraquinone gives a yellow vat dye, and further condensation with 1-aminoanthraquinone gives an orange-red dye, in which two 1,2′-dianthrimide residues are united by a carboxylamide group.[62]



Indanthrene Corinth RK



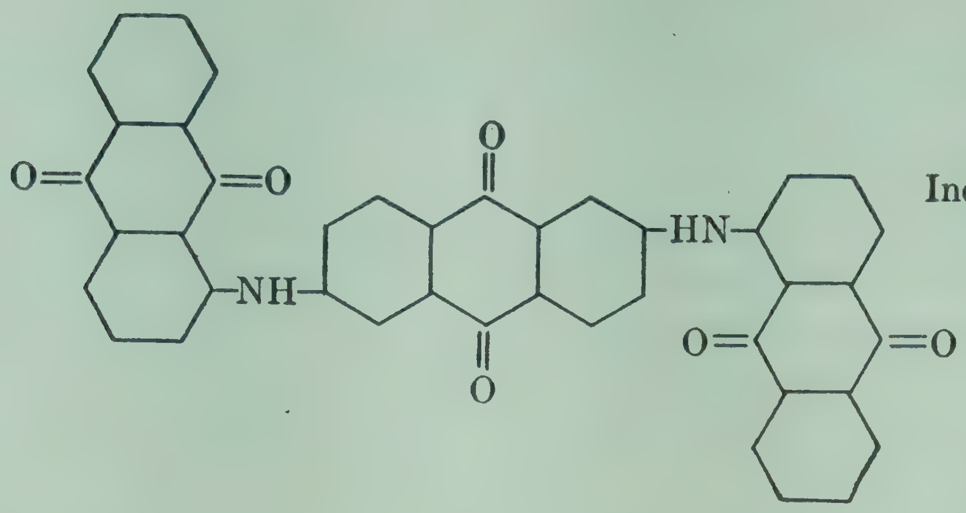
(I)

The nitration of 1,1′-dianthrimide with mixed acid in presence of boric acid at about 25° gives the 4,4′-dinitro compound, reduced by means of sodium sulfide and caustic soda to the diamine (I). The dibenzoyl derivative of (I), marketed at one time as Algol Gray B, is now the intermediate for the carbazole dye, Indanthrene Olive R.

The condensation of two moles of 1-aminoanthraquinone with one of 2,6- and 2,7-dichloroanthraquinone respectively gives two useful dyes, Indanthrene Orange 7RK (formerly Indanthrene Red G) (Isler and Kačer, 1907) (BASF; CI 1140) and Indanthrene Red R (BASF; CI 1142). The isomeric trianthrimide from 2-chloroanthraquinone and 1,5-diaminoanthraquinone appears to have been marketed at one time as Indanthrene Bordeaux B (Indanthrene Claret B; Anthra Claret RT; CI 1146), but Indanthrene Bordeaux B in the current IG range is differently constituted (see later). Algol Bordeaux RT (ST 1255; CI 1143) (formerly Indanthrene Bordeaux B extra) is prepared by condensing 6-chloro-1-

[61] Beard and du Pont, USP 2,133,072.

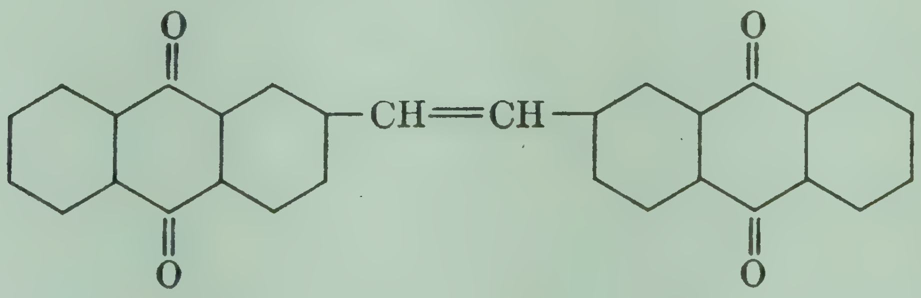
[62] Deinet and du Pont, USP 2,129,993.

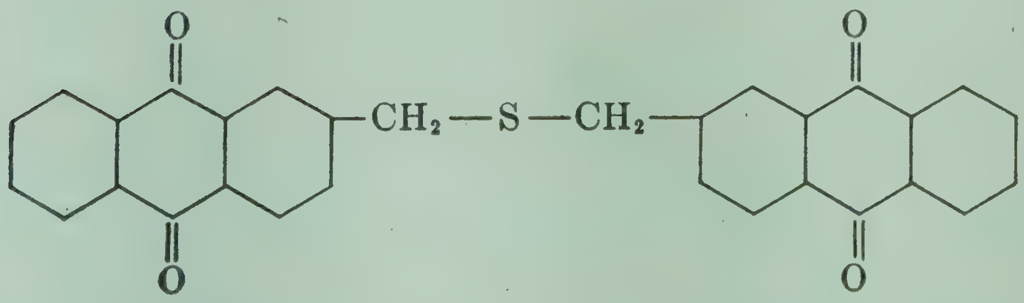

Indanthrene Orange 7RK

aminoanthraquinone with 2,7-dichloroanthraquinone in nitrobenzene solution in presence of sodium carbonate and copper oxide. A bordeaux dye of more bluish tone, Algol Bordeaux 3B (CI 1141), is obtained by condensing two moles of 1-amino-4-methoxyanthraquinone with one of 2,6-dichloroanthraquinone. Indanthrene Grey K has been stated (CI 1145) to be the 4′,4″-diamine prepared by nitration and reduction of the trianthrimide obtained from 1,5-diaminoanthraquinone and 1-chloroanthraquinone, and more recently, to be the product of the treatment of 4,4′-bisbenzamido-1,1′-dianthrimide with 96% sulfuric acid at 8°.[63] Grey K does not appear in the latest IG shade card of Indanthrenes.

MISCELLANEOUS SIMPLE DERIVATIVES OF ANTHRAQUINONE

1,2-Benzanthraquinone, prepared by the condensation of naphthalene and phthalic anhydride in presence of aluminum chloride and cyclization with sulfuric acid, has no dyeing properties; but it has been used as a pigment, Sirius Yellow G (Elbs, 1886) (BASF; CI 1094). Anthraflavone G (Isler, 1905) (BASF; CI 1095), which is now obsolete because of its low fastness to light (3–4) and its tendering action on cellulose, was formerly valued for the relatively fast green shades obtained by admixture with


Anthraflavone


(I)

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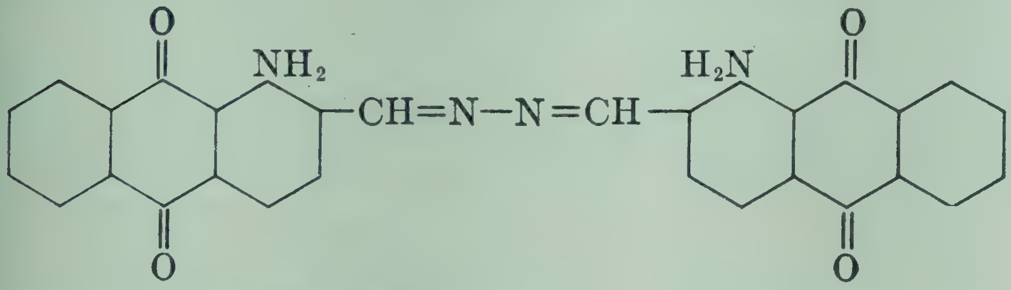
[63] Microfilm FD 2537/46.

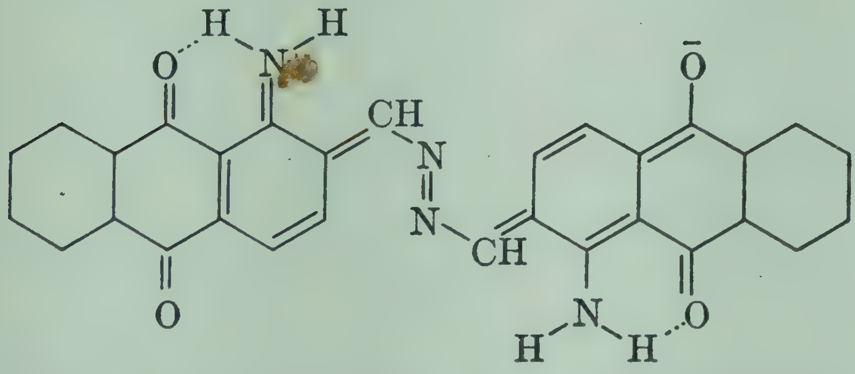
Indanthrene Blue. It may be prepared by fusion of β-methylanthraquinone with caustic potash and alcohol at about 170°, or by the action of copper powder on β-dichloromethylanthraquinone in nitrobenzene solution. An interesting method of preparation is to heat di-β-anthraquinonyldimethyl sulfide (I) (readily obtained by the interaction of β-chloromethylanthraquinone and sodium sulfide) above its m.p. (249–250°), when hydrogen sulfide is lost with the formation of Anthraflavone. Such a reaction appears to be involved in the occurrence of Anthraflavone in Cibanone Yellow R, the dye prepared by the thionation of β-methyl- or β-chloromethylanthraquinone.[64]

When 1,1′-dichloro-2,2′-dianthraquinonylethylene is treated with primary aromatic amines, the products are gray, violet, brown or red-brown in shade, and are fast to chlorine, washing and water-spotting.[65]

Indanthrene Bordeaux B (Isler and Kačer, 1906) (BASF; CI 1146), stated[18] to be the trianthrimide obtained by the condensation of 2-chloroanthraquinone with 1,5-diaminoanthraquinone, has now been shown to be 1-aminoanthraquinone-2-aldazine.[2, 16] The color and stability of the compound are associated with resonance structures such as (II). Two methods of preparation may be used.[66, 67] When 1-nitro-2-methylanthraquinone is heated with aluminum chloride or treated with chlorosulfonic acid and 65% oleum at 0°, anthraquinone-1,2-isoxazole (III) is formed; (III) is not isolated, but submitted directly to reductive hydrolysis by diluting the sulfuric acid solution, adding ferrous sulfate and boiling. The product is 1-aminoanthraquinone-2-aldehyde (IV), which is condensed with hydrazine sulfate in sodium sulfite solution at the



Indanthrene Bordeaux B



(II)

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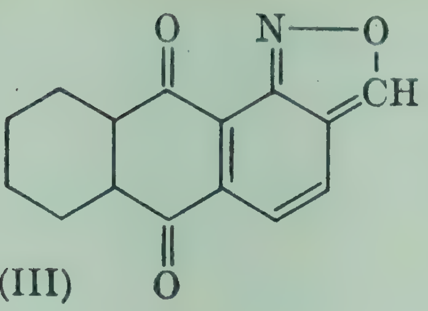
[64] See Chapter XXXVI.

[65] IG, DRP Anm. J. 53,676.

[66] Ruggli and Henzi, *Helv. Chim. Acta* **13,** 409 (1930).

[67] Cassella, DRP 343,064; BP 148,339; 346,188; 357,042; MLB, DRP 360,422; 364,181; IG, DRP 479,350.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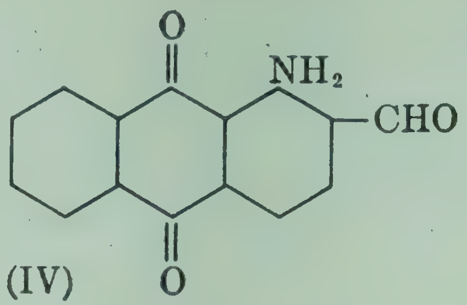
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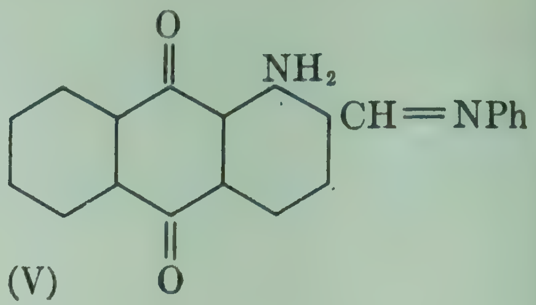
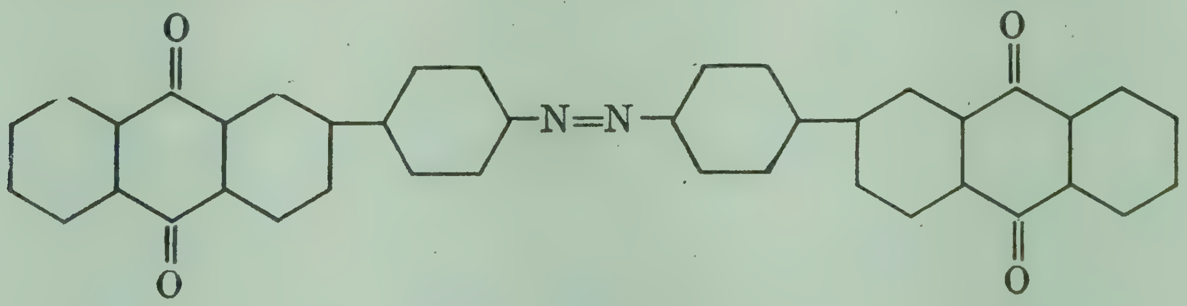

(V)

boil to form the dye. A second method is to heat 1-amino-2-methylanthraquinone with nitrobenzene in presence of anhydrous potassium carbonate; the azomethine (V) which is thus formed gives (IV) on acid hydrolysis. Indanthrene Bordeaux B dyes claret-red shades from an intense olive-green vat; the fastness to light is 6–7 and to chlorine 4. The dye is unaltered by prolonged boiling with 20% alcoholic potassium hydroxide and is substantially unaffected by boiling for several hours with concentrated hydrochloric acid; it is hydrolyzed to (IV) by boiling with 65% sulfuric acid, and converted into 1-aminoanthraquinone-2-carboxylic acid by heating with concentrated sulfuric acid at 160°. An interesting property of Indanthrene Bordeaux B is its sensitivity to nitrous acid; when the dye is dissolved in glacial acetic acid and sulfuric acid and treated with sodium nitrite at 0–5°, fission of the aldazine linkage takes place, together with diazotization of the amino groups. As a result, the azo dye obtained by coupling the diazonium solution with β-naphthol is identical with the dye from diazotized 1-aminoanthraquinone-2-aldehyde; attempts to replace the diazonium groups by hydroxyl and chlorine lead to 1-hydroxy- and 1-chloroanthraquinone-2-aldehyde, and treatment of the diazonium solution with alkaline formaldehyde gives a mixture of anthraquinone-2-carbinol and -2-carboxylic acid by the Cannizzaro reaction taking place on anthraquinone-2-aldehyde.

Among the acids used for acylating aminoanthraquinones, azobenzene-4,4′-dicarboxylic acid has been mentioned, and attention was drawn to the stability of the azo linkage to alkaline hydrosulfite which enables the products to be applied as vat dyes. Since such dyes have excellent light fastness, azo compounds of other types have been prepared. Azobenzene-4,4′-dicarboxylic acid reacts with *o*-aminohydroxy- or *o*-aminomercaptoanthraquinones to form oxazoles or thiazoles.[68] Aminoazo


(VI)

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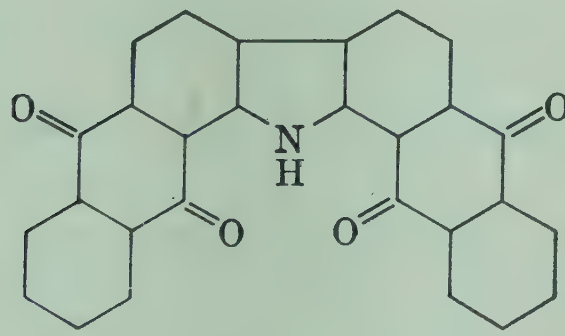
[68] IG, BP 487,380.

compounds have been acylated with vattable carboxylic acids, e.g., diaminoazobenzene with anthraquinone-2-carboxyl chloride.[69] Methods for the production of azo dyes by reducing aromatic nitro compounds or oxidizing primary arylamines have been applied to anthraquinone derivatives; e.g. 2-*p*-nitrophenylanthraquinone is converted into 4,4′-dianthraquinonylazobenzene (VI), which is a yellow vat dye.[70]

CARBAZOLE DERIVATIVES

Anthraquinone vat dyes containing the carbazole nucleus follow the anthrimides logically, since the latter are the penultimate intermediates from which the carbazoles are prepared by a simple cyclization process. These carbazole derivatives as a class are level-dyeing and possess excellent all-round fastness, and they include some of the most largely used anthraquinone vat dyes. The shades are yellow, orange, khaki, brown, and olive.

Mieg (1910) discovered that 1,1′-anthrimides, which were of little or no value in themselves as dyes, underwent by treatment with aluminum chloride or caustic potash ring closure to carbazoles which had greatly improved dyeing and fastness properties.[71] Thus 1,1′-dianthrimide itself, completely valueless as a dye, gives the bright orange-yellow dye, Indanthrene Yellow FFRK. The dicarbazoles (from the trianthrimides) and the tetracarbazole (from pentanthrimide), especially the last, Indanthrene Khaki GG, are valuable dyes. Indanthrene Khaki GG, which gives a greenish tone of khaki with excellent fastness to all agencies, is one of the major products of the dyestuff industry during war time, and the United States production in 1943 was over 10 million pounds (12.5% strength) of the value of over $11,000,000. One result of increasing the number of anthraquinone residues in the anthrimide and carbazole series of dyes is to improve the fastness to alkali boil. When only one anthraquinone nucleus is present as in some of the acylamidoanthraquinones or



Indanthrene Yellow FFRK

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[69] IG, FP 826,768.

[70] IG, BP 502,149; 503,556.

[71] MLB, DRP 240,080; Mieg and IG, DRP 451,495; 464,292; 470,550; Baumann and IG, DRP 513,227.

the anthraquinoneacridones, reduction to the soluble leuco form is likely to occur during kier boiling by the action of alkali and reducing agents such as hydrolytic products of starch. When the dye is built up of more than one anthraquinone nucleus, the additional quinone groups act as oxidizing agents and restrain the reduction and consequent bleeding of the dye in the kier.

An important advance was made when it was observed that anthrimides containing benzamido groups in the 4- or 5-position with reference to the imino group cyclized much more readily than the parent anthrimides; agitation with concentrated sulfuric acid is adequate for the purpose, and the resultant dyes are brighter and have better tinctorial power. The mechanism of the reactions which take place when a polyanthrimide is treated with sulfuric acid or aluminum chloride or caustic potash, and subsequently with an oxidizing agent, such as sodium hypochlorite, which is essential for the development of the pure shade, has not been fully elucidated; the structures assigned to some of the dyes in this group are plausible, rather than conclusively proved. Thus some hydrolysis of the benzamido groups might take place,[72] and with polyanthrimides all the cyclizations to form the corresponding polycarbazole may not take place.[72a] Indanthrene Brown R (CI 1151) and similar dyes were at one time assigned acridine structures, but they are now considered to be carbazoles.

Preparation. The general procedure[3] for the conversion of unsubstituted anthrimides to carbazoles (e.g., 1,1′-dianthrimide to Indanthrene Yellow FFRK; pentanthrimide to Indanthrene Khaki 2G) is to heat a mixture of the anthrimide (4 parts) and aluminum chloride (8 parts) to about 160°, add sodium chloride (1 part) and continue heating until the melt solidifies. The temperature is then raised till the charge becomes fluid, the temperature required for different anthrimides varying from 150° to 250°; at this stage the reaction is exothermic and proceeds rapidly to completion in the course of a few minutes. The melt is poured into water or dilute hydrochloric acid, boiled up, filtered and washed. There are by-products formed in the reaction, and their removal by a vigorous oxidation with dichromate and dilute sulfuric acid or alkaline hypochlorite is essential for obtaining the true shade of the dye. Thus, for Indanthrene Yellow FFRK, the wet paste is mixed with caustic soda solution and treated with hypochlorite (10–12% chlorine) at 80–85° until a test for chlorine persists after four hours. This takes about 20 hours, when the dye is filtered off and submitted to a second oxidation, in which it is agitated with water and nitrobenzene, and treated alternately with hypochlorite and permanganate, until a visual examination of the dye indicates that the standard shade has been produced. The orange dicarbazole (I), prepared by aluminum chloride cyclization of 1,1′,5,1″-trianthrimide (II), is contaminated with a monochloro-1,1′-dianthrimide-2,2′-carbazole, and (I) may be separated by slurrying the reaction product with 95–98% sulfuric acid at 100–110° and filtering off the sparingly soluble sulfate of (I).[73] The sodium-aluminum chloride fusion of trianthrimides may be carried out in presence of nitrobenzene or potassium *m*-nitrobenzenesulfonate at 110–160°.[74] Trichlorobenzene as solvent for carbazolization with aluminum chloride is stated to give dyes with improved shade and brightness.[75]

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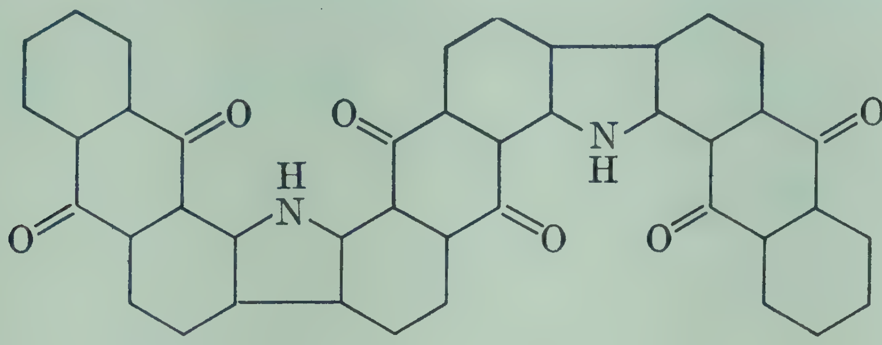
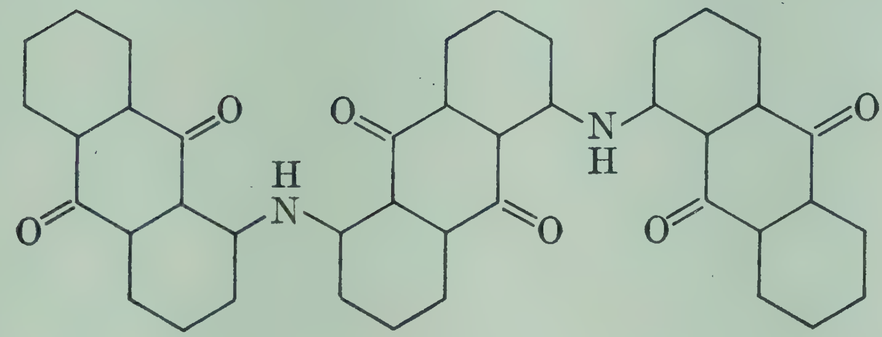
[72] Baumann and IG, DRP 491,428.

[72a] While 1,1′, 5,1″-trianthrimide gives a yellow dye by fusion with aluminum chloride, ethanolic caustic potash yields an olive dye; Kuhlmann, BP 591,979.



(I)



(II)

Anthrimides can be cyclized to carbazoles by refluxing in a suitable solvent (e.g., *o*-dichlorobenzene) with titanium tetrachloride. Excess titanic chloride is distilled off, the slurry is vatted, aerated, and oxidized with hypochlorite.[76] The carbazole from 1,2′-dianthrimide, an orange-red dye, is prepared in this manner.

The general procedure for carbazolizing anthrimides containing benzamido groups is to dissolve the anthrimide in five times its weight of sulfuric acid monohydrate at 30°, and add 78% sulfuric acid during a few hours. The precipitated dye is filtered and oxidized with about 1% aqueous sodium chlorate, or dichromate and dilute sulfuric acid, at about 90° for a few hours. Thus Indanthrene Golden Orange 3G (Chart 1) is prepared by dissolving the anthrimide (III; 400 kg.) in 96% sulfuric acid (1040 kg.) and 20% oleum (1040 kg.) at 30°, and adding 78%

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[73] Scalera and American Cyanamid, USP 2,421,163.

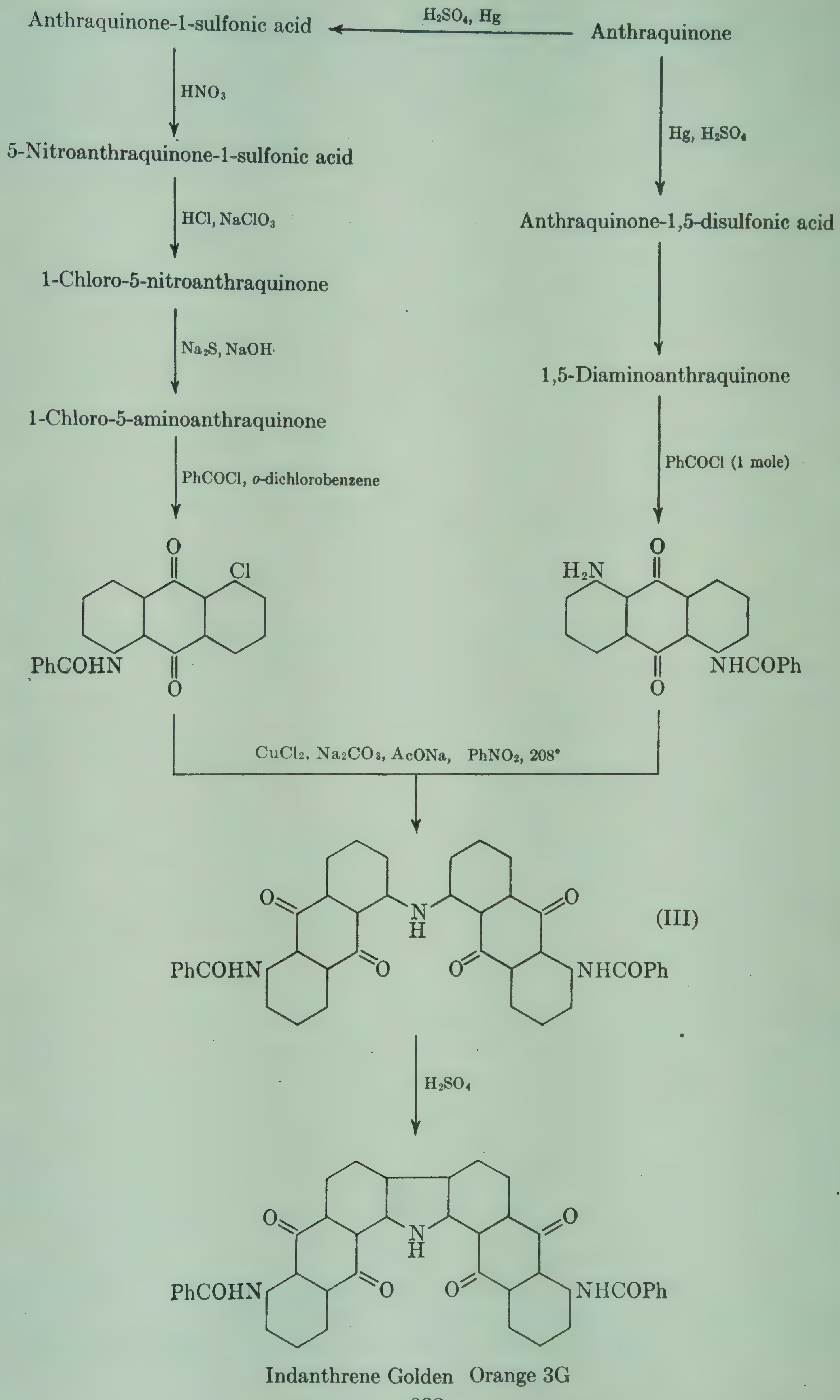
[74] du Pont, BP 572,428; see also Scalera and American Cyanamid, USP 2,432,972.

[75] Smyth, Cullinan and American Cyanamid, USP 2,434,056.

[76] Lecher *et al.*, USP 2,416,931; BP 594,907; see also Ciba, BP 585,798.

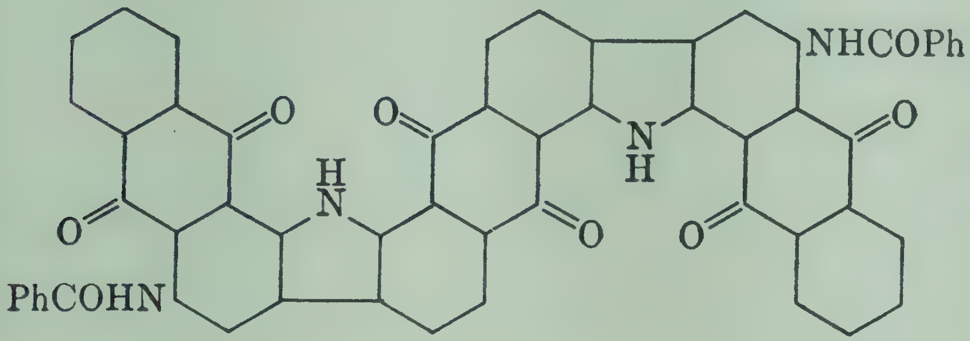
CHART 1

Preparation of Indanthrene Golden Orange 3G


Anthraquinone-1-sulfonic acid
H2SO4, Hg
Anthraquinone
HNO3
Hg, H2SO4
5-Nitroanthraquinone-1-sulfonic acid
HCl, NaClO3
Anthraquinone-1,5-disulfonic acid
1-Chloro-5-nitroanthraquinone
Na2S, NaOH
1,5-Diaminoanthraquinone
1-Chloro-5-aminoanthraquinone
PhCOCl, o-dichlorobenzene
PhCOCl (1 mole)
O
Cl
PhCOHN
O
O
H2N
NHCOPh
O
CuCl2, Na2CO3, AcONa, PhNO2, 208°
O
N
H
O
(III)
PhCOHN
O
O
NHCOPh
H2SO4
O
N
H
O
PhCOHN
O
O
NHCOPh
Indanthrene Golden Orange 3G

sulfuric acid (2740 kg.) in 6–10 hours. The precipitated dyestuff is filtered and washed with 85–87% sulfuric acid (1200 kg.). The press cake is mixed with 86% sulfuric acid (500 kg.), added to sodium dichromate (70 kg.) in water (6000 l.), and heated at 90° with direct steam for 5 hours. Sodium bisulfite is added; the dyestuff is filtered and washed.

In the cyclization of certain anthrimides to carbazoles by means of aluminum chloride, the addition of sulfur dioxide or an alkali bisulfite is an advantage.[77] The liquid complex from aluminum chloride and sulfur dioxide may be used together with sodium chloride.[78] Thus, for the carbazolization of the trianthrimide from 1-chloro-4-benzamidoanthraquinone and 1,5-diaminoanthraquinone to form Indanthrene Red Brown GR, the reagent employed is a mixture of aluminum chloride and sodium chloride into which sulfur dioxide is blown in; the mixture becomes fluid at 40° and the cyclization is complete in one hour at 85°. The mixed imides from an acylamidoanthraquinone and an acridone or thioxanthone can be cyclized with aluminum chloride and sulfur dioxide at as low as 90°, and clearer red-brown dyes are obtained than by the older method using aluminum chloride in nitrobenzene solution. Even below 50° a mixture of aluminum chloride and sodium bisulfite yields the same dyes.[79] The use of aluminum chloride in an acid chloride (e.g., thionyl or benzoyl chloride) induces cyclization at very low temperatures, and in presence of an excess of acid chloride no hydrolysis of acylamido groups takes place.[80] The molecular compound of aluminum chloride and an aromatic nitrile is another useful cyclizing agent for anthrimides containing acylamido groups.[81] The anthraquinonecarbazole dyestuffs, generally prepared by cyclization involving the loss of hydrogen to form a C—C link, can be synthesized by other methods. An *o*-aminoarylaminoanthraquinone may be diazotized and heated with an organic solvent and a base. The reaction has been applied to products of vary-



Indanthrene Red Brown GR

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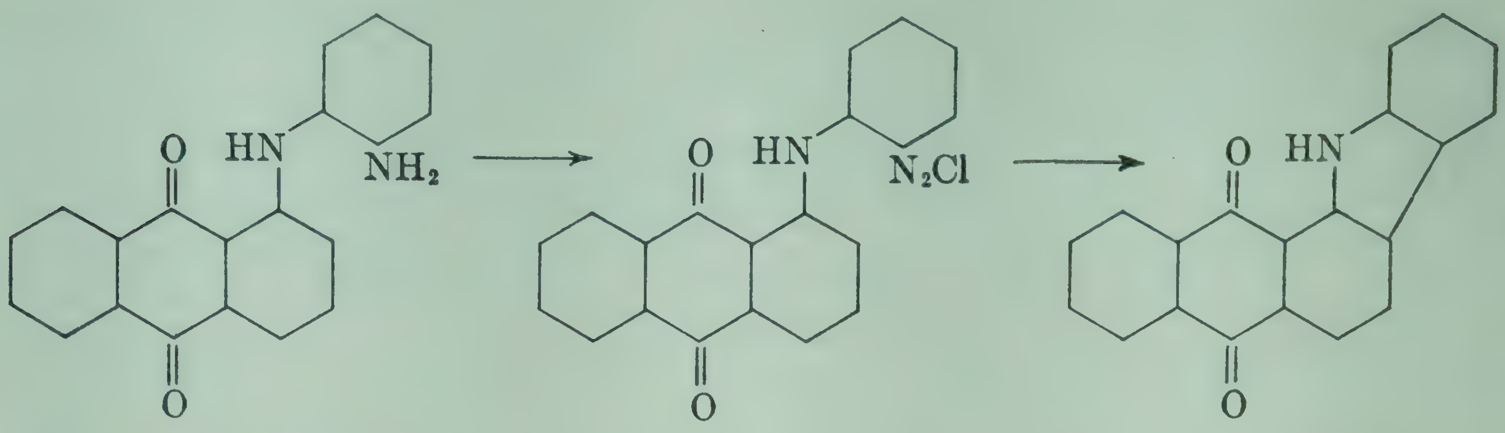
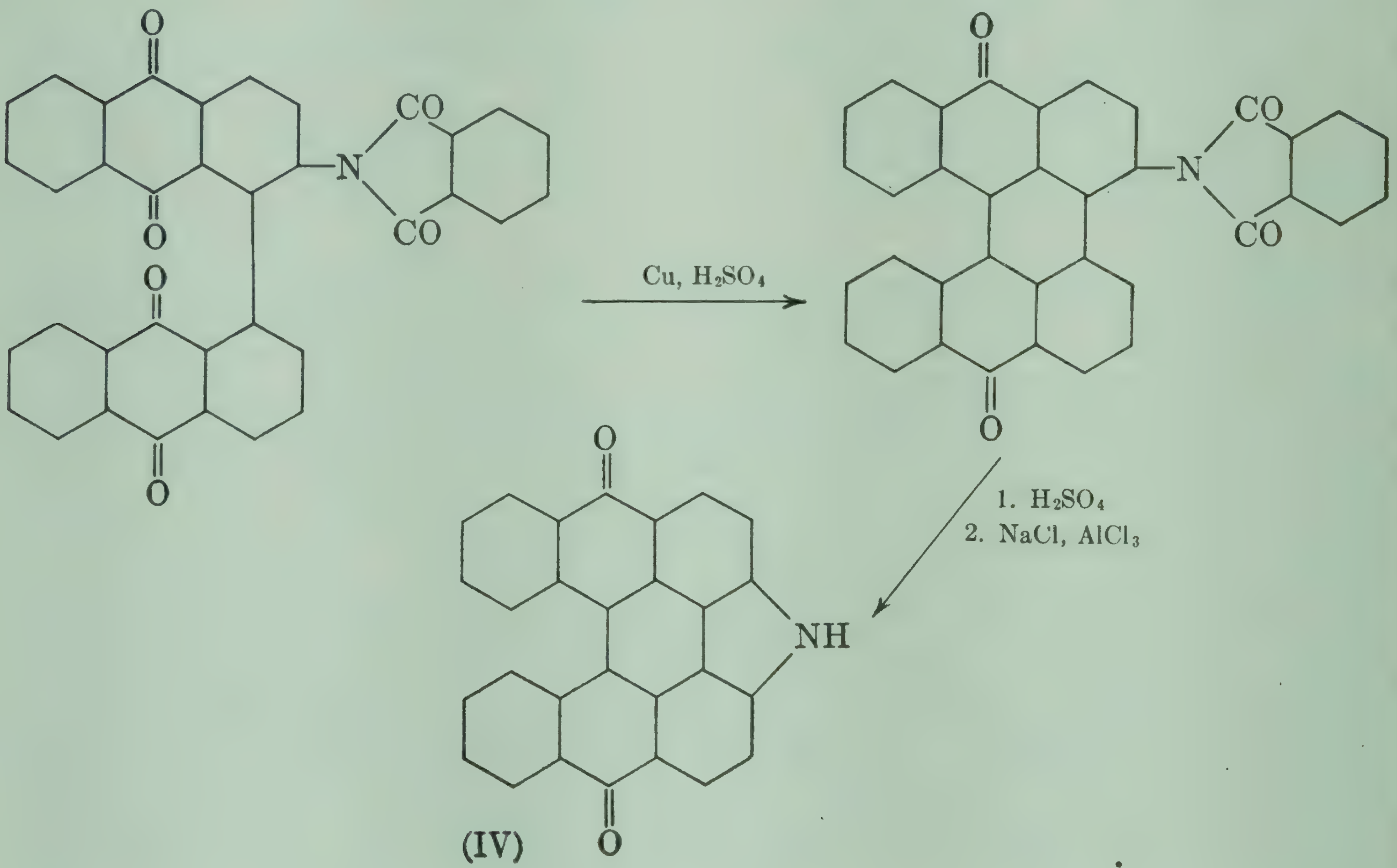
[77] Wieners and Mieg, USP 2,212,965.
[78] IG, FP 843,525.
[79] IG, BP 519,123.
[80] IG, BP 461,432.
[81] IG, BP 497,971.



ing complexity and yields yellow, brown, olive, and gray vat dyes.[82] In another method, 2-amino-1,1′-dianthraquinonyl is heated with sodium-aluminum chloride at 150°; cyclization to a carbazole takes place and an olive vat dye is obtained.[83] This can be applied to the production of carbazoles of the *ms*-benzo- or naphthodianthrone type such as (IV). When 1-arylaminoanthraquinones in which an *ortho* or *peri* position to the imino group is substituted by halogen, the other being unsubstituted, are heated with acid-binding agents, ring closure takes place. When the aryl group is a benzene derivative, carbazoles are formed; but when the aryl is di- or polycyclic, the products are greenish-blue and brown vat dyes of the acridine type. Some of the products have been sulfonated to obtain wool dyes.[84]



(IV)

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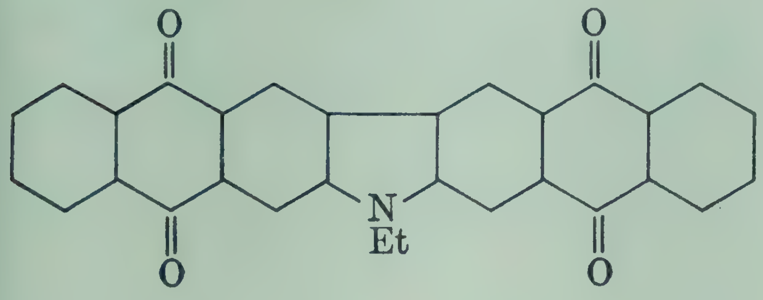
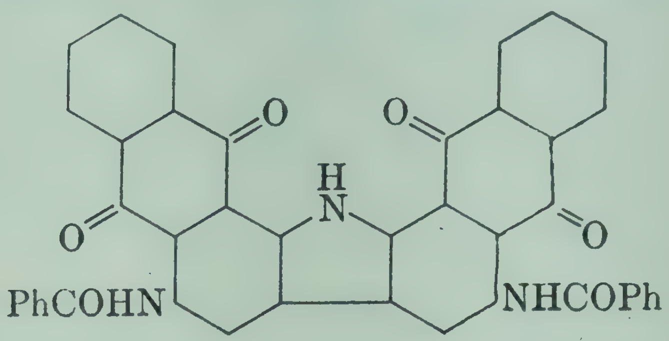
[82] Ciba, BP 433,574.
[83] Ciba, FP 786,105.
[84] IG, BP 443,958–9.

Constitution and shades. The simplest member of the series is Indanthrene Yellow FFRK, which has the fastness properties characteristic of the series, but is a tenderer.[1a] The *N*-ethyl derivative of the linear isomer, prepared by condensing phthalic anhydride with *N*-ethylcarbazole and cyclizing to the bisanthraquinone, was marketed at one time as Hydron Yellow G, C or NF (Nissen and Saul, 1911) (C; CI 1159); but the dye is now obsolete, although the shade on cotton has been stated to be very fast, especially to light. Indanthrene Golden Orange 3G (BASF, 1924),[85] Indanthrene Brown R, and Indanthrene Olive R (Mieg, 1910) are derivatives of Indanthrene Yellow FFRK with benzamido groups in the 5,5′-, 4,5′- and 4,4′-positions. Indanthrene Golden Orange 3G is not a tenderer.[1a] Indanthrene Olive 3G is an analog of Indanthrene Olive R, in which the chloride of anthraquinone-2-carboxylic acid replaces benzoyl chloride. By starting with 6,6′-dichlorodianthrimide and nitrating, reducing, benzoylating, and cyclizing with sulfuric acid to the carbazole, the olive dye has better fastness properties than the unchlorinated compound.[86] A purified brand of Indanthrene Brown R, obtained by treatment with 88% sulfuric acid and then with dichromate and acid, is marketed as Indanthrene Brown FFR.[3] When the dianthrimides obtained by condensing a mixture of 1-amino-5- and 8-benzamidoanthraquinone with 1-chloro-4-benzamidoanthraquinone in nitrobenzene solution are treated, without isolation, with aluminum chloride, a bright brown carbazole dye of good fastness to light and chlorine is obtained in high yield.[87] The introduction of a methoxyl group in Indanthrene Brown R gives Indanthrene Red Brown 5RF, which is prepared by the carbazolization of the anthrimide from 1-chloro-5-benzamido-8-methoxyanthraquinone and 1-amino-4-benzamidoanthraquinone.[3]



Hydron Yellow G



Indanthrene Olive R

Indanthrene Orange 2RN is a new IG dye, stated to be cheaper to manufacture and to have better fastness properties than Indanthrene Orange 2R. Its constitution is interesting as a derivative of 1,2-phthaloylcarbazole-8-carboxylic acid.[24]

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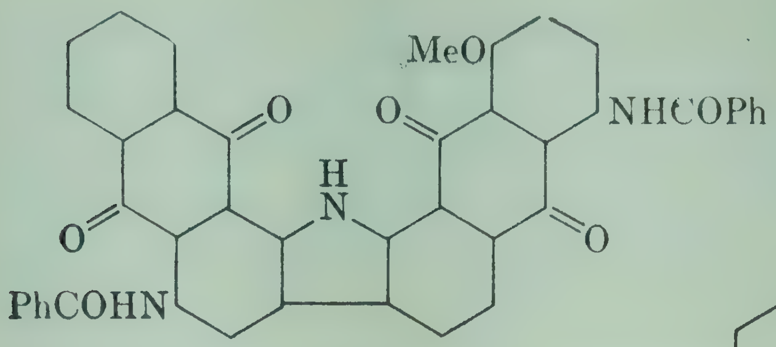
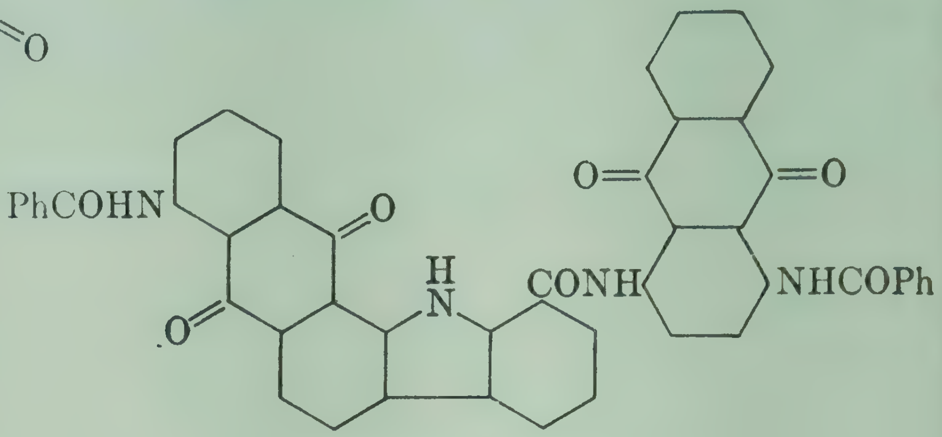
[85] Cf. du Pont, BP 513,281; Schmidt, *Z. angew. Chem.* **41**, 42 (1928).

[86] Dettwyler and du Pont, USP 2,111,092.

[87] Scalera, Stewart and American Cyanamid, USP 2,425,126.

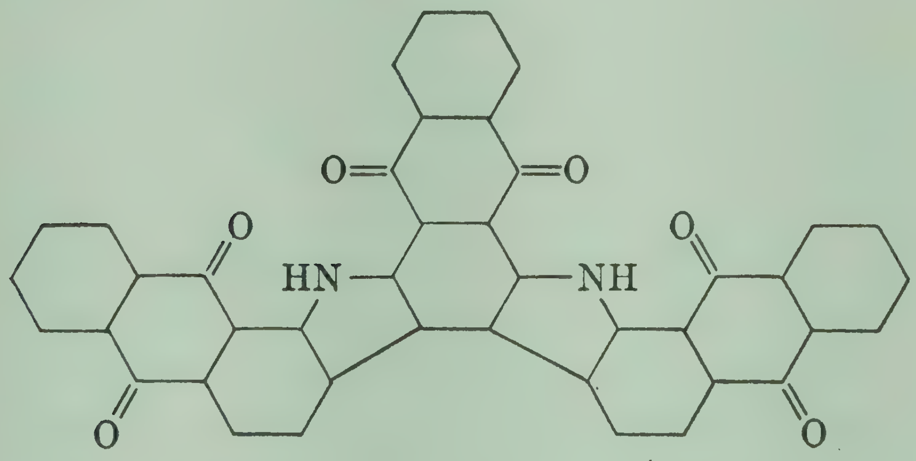


Indanthrene Red Brown 5RF

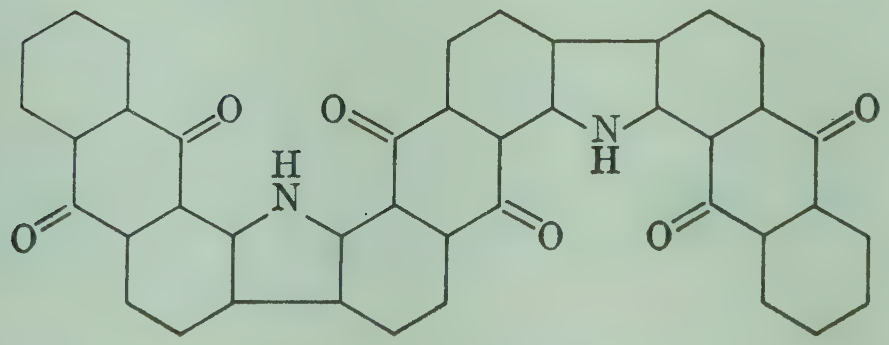


Indanthrene Orange 2RN

Trianthrimides and their benzamido derivatives yield dicarbazoles, which constitute a series of useful vat dyes. Examples are Indanthrene Brown GR (Uhlenhuth, 1908) (from 1,1′,4,1″-trianthrimide), Yellow 3R (from 1,1′,5,1″-trianthrimide), and Indanthrene Red Brown GR, which is the 4′,4″-dibenzamido derivative of Yellow 3R, prepared by the carbazolization of the anthrimide from one mole of 1,5-diaminoanthraquinone condensed with two moles of 1-chloro-4-benzamidoanthraquinone. Indanthrene Yellow 3RT is not one of the very active tenderers.[1a] Indanthrene Yellow 3R is a purified form of Indanthrene Yellow 3RT.[87a] A purer brand of Indanthrene Brown GR is marketed as Indanthrene Brown BR. The cyclization of the trianthrimide to



Indanthrene Brown GR



Indanthrene Yellow 3R (3RT)

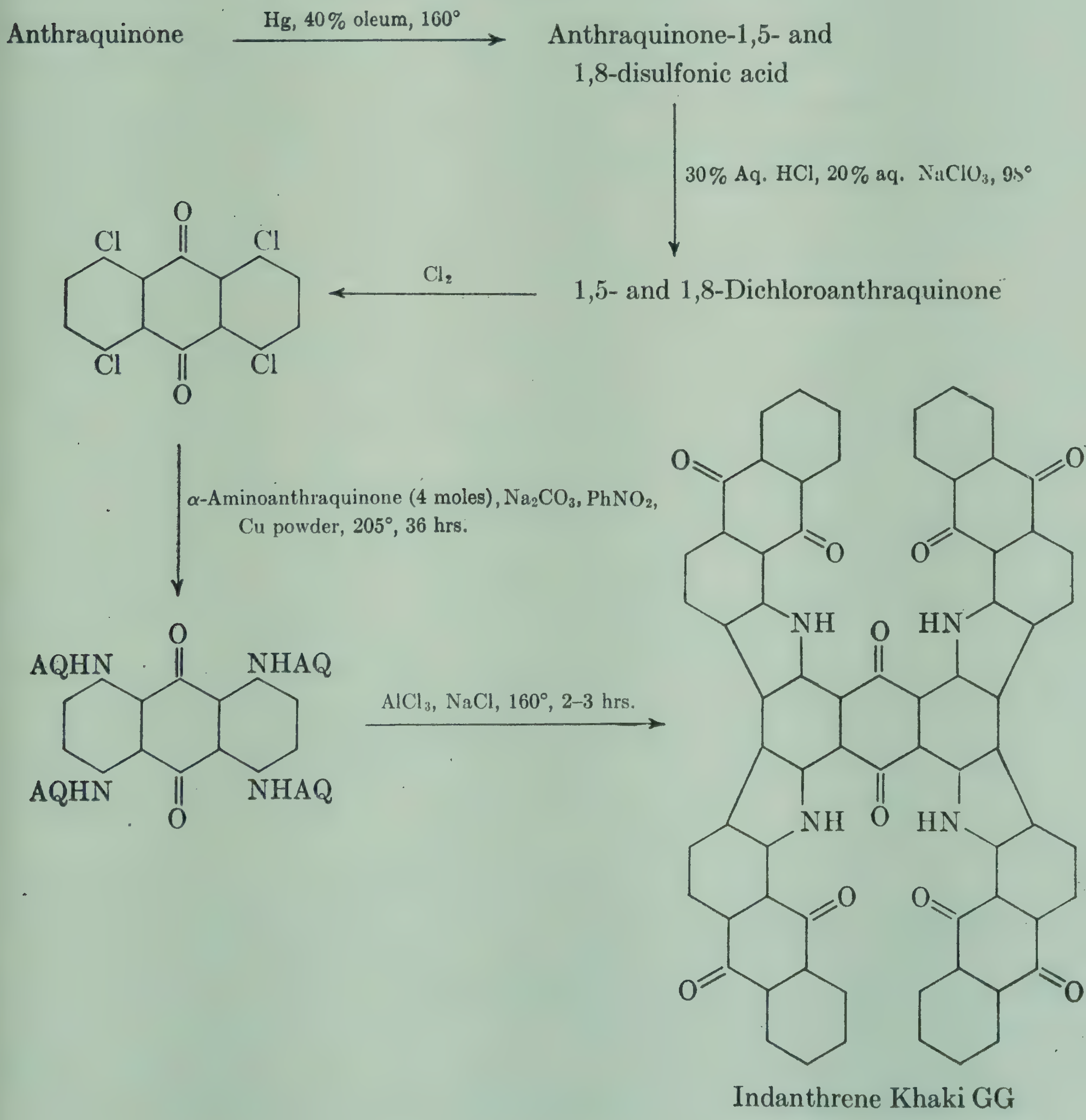
[87a] According to Ref. 18, Indanthrene Yellow 3R is the isomer from 1,8-diaminoanthraquinone.

Indanthrene Brown BR is effected in a pyridine base, b.p. 140–144°, with aluminum chloride at 135°.

Indanthrene Khaki GG (MLB; 1911) is an important dye, usually formulated as a tetracarbazole (see Chart 2 for preparation). There is some doubt, however, if all the four anthrimide groups undergo cyclization under the conditions of the aluminum chloride-sodium chloride treatment. Indanthrene Khaki GG shades are markedly olive in tone in comparison with the usual mineral khaki shades; for obtaining the correct shade and level results, the temperature of vatting and dyeing must not exceed 60°, glue must be added to the dyebath, and the dyed material must be soured with 0.1–0.2% formic or sulfuric acid before soaping. A greenish olive dye with excellent fastness properties, allied

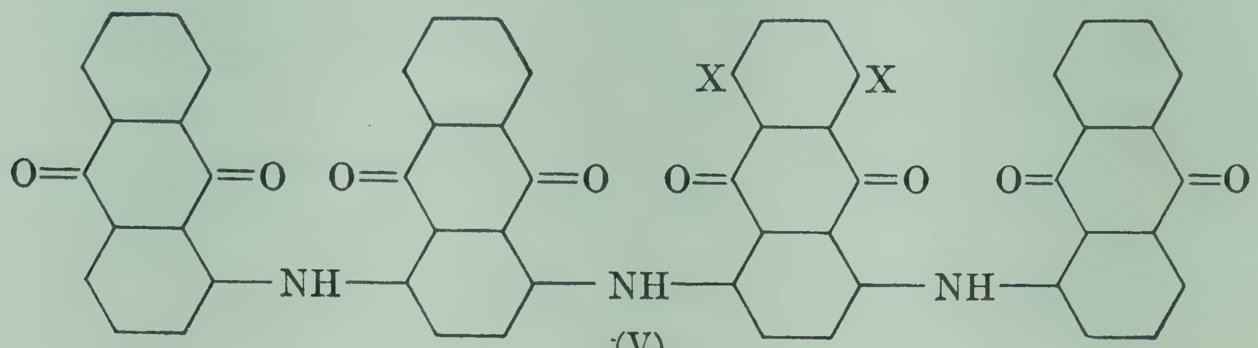
CHART 2

PREPARATION OF INDANTHRENE KHAKI GG



Anthraquinone
Hg, 40% oleum, 160°
Anthraquinone-1,5- and 1,8-disulfonic acid
30% Aq. HCl, 20% aq. NaClO₃, 98°
1,5- and 1,8-Dichloroanthraquinone
Cl₂
Cl
Cl
Cl
Cl
O
O
α-Aminoanthraquinone (4 moles), Na₂CO₃, PhNO₂, Cu powder, 205°, 36 hrs.
AQHN
NHAQ
AQHN
NHAQ
O
O
AlCl₃, NaCl, 160°, 2–3 hrs.
NH
HN
NH
HN
O
O
Indanthrene Khaki GG

in constitution to Indanthrene Khaki GG, is prepared by the carbazolization of the pentanthrimide (V), in which one X is an α-anthraquinonylamino group and the other X is hydrogen.[88]



(V)

The interest in the anthraquinonecarbazole series, especially the complex dyes of brown, black-brown and gray shades, is shown by the large number of patents on the subject.[89] The presence of benzamido groups containing alkyl- or aryl-sulfonyl substituents in anthrimides and anthraquinonecarbazoles gives dyes with improved fastness and printing properties.[32, 90] "A pure brown-red dye" is obtained by condensing 1,4-diaminoanthraquinone (48) simultaneously with 1-chloroanthraquinone (48) and 1,5-dichloroanthraquinone (28), and carbazolizing the product.[91] 1,4-Dichloro-5-benzamidoanthraquinone is condensed with two moles of an α-aminoanthraquinone, and the trianthrimide is carbazolized.[92] 1,4-Dichloroanthraquinone-6-carboxyl chloride is condensed with 1-amino-4- or 5-benzamidoanthraquinone, and cyclized with aluminum chloride in nitrobenzene, or with sulfuric acid and sodium dichromate, to cold-dyeing browns.[93] Using 1-bromo-4-acylamido-3-methylanthraquinone as the primary intermediate, browns of clearer shades than in the absence of the 3-methyl group are obtained.[94] Brown vat dyes of good fastness are obtained by condensing 1,6-dichloroanthraquinone with one mole of an α-aminoanthraquinone, cyclizing the 1,1′-dianthrimide to the carbazole, and condensing the remaining halogen with an α-aminoanthraquinone, aminoanthraquinoneacridone, aminopyridanthrone, etc.[95] By condensing 5-amino-2,1(*S*)-anthraquinonethioxanthone with 1-chloro-4 or 8-benzamidoanthraquinone, cyclizing by aluminum chloride fusion in pyridine or nitrobenzene, and oxidizing finally, the dyes are orange to red in shade, are fast to bleaching, and have printing properties.[96] Two aminodianthrimide residues may be joined by acylation with a dibasic carboxylic acid and cyclized to carbazoles;[97] thus terephthaloyl-bis-(5-amino-5′-benzamido-1,1′-dianthrimide) yields an orange-yellow vat dye.[98] 1,2-Phthaloylcarbazolemonocarboxylic acids are used to acylate aminoanthraquinones, yielding fast yellow, orange and red dyestuffs, which may be also obtained if the aminoanthraquinone is acylated with a suitable acylamidoanthraquinonecarboxylic acid and the product then cyclized.[99] Indanthrene Olive R may be partly debenzoylated and the product reacylated with 1,9-anthraisothiazole-3-carboxylic acid to obtain an olive green vat dye with excellent fastness;[100] if the partially debenzoylated substance is acetylated and cyclized, e.g., with acetic acid and oleum, a dark brown vat dye is obtained, which may be a 1,9-pyridone.[101] Cyclization of 8′,8″-dibenzamido-1,1′,4,1″-trianthrimide, prepared from 1,4-diaminoanthraquinone and 2 moles of 1-chloro-8-benzamidoanthraquinone, with aluminum chloride in presence of a tertiary base gives a red-brown vat dye, particularly fast to light.[102] Vattable compounds containing pyridino or pyridono rings and substituted by arylamino groups have been cyclized to obtain yellow, olive-brown, blue-green or gray shades according to the complexity of the molecule.[103] Thus acridone-carbazole vat dyes are yellow, gray, khaki, brown and black; the fast deep shades are specially useful in printing and for the formation of leuco sulfuric esters.[104]

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[88] Smyth and American Cyanamid, USP 2,385,113.

[89] E.g., see Ciba, BP 433,090; BP 414,529; IG, DRP Anm. J. 48,774; BP 410,552.

[90] Ciba, SP 232,597; 236,683–8; 242,509–11; 244,765; USP 2,453,232.

[91] Ciba, BP 580,642; Kuhlmann, BP 602,610.

[92] Ciba, BP 585,798; USP 2,459,424; 2,473,949–50.

[93] Graham and du Pont, USP 2,152,186.

[94] Deinet and du Pont, USP 2,162,196.

[95] Lulek, Dettwyler, and du Pont, USP 2,203,227; du Pont, BP 542,594.

Ciba synthesize a series of dyes by condensing 3-chloro- or 3-bromo-1-acylamidoanthraquinone with amines, amides and mercaptans, especially with 1-amino-4- or 5-benzamidoanthraquinones;[105] 1,3-dihalogenoanthraquinones can be condensed in the same way.[106] A more complicated dye is obtained when 1,3-dichloroanthraquinone is condensed with two moles of 1,4-diaminoanthraquinone, the product condensed again with two moles of α-aminoanthraquinone, and finally heated with aluminum chloride in pyridine. The final product probably contains five anthraquinone and two carbazole nuclei and such dyes give dark shades such as blackish-olive.[107] When dihalogenoanthraquinones are condensed with aminodiphthaloyl-carbazoles and the products cyclized, fast brown and maroon dyes are obtained.[108]

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[96] Dettwyler and du Pont, BP 561,754. See also Max, Randall, and General Aniline and Film, BP 621,705.

[97] Lulek, Belcher, and du Pont, USP 2,045,304.

[98] Lulek, Belcher, and du Pont, USP 2,124,165.

[99] IG, BP 467,971.

[100] Irving, Shaw, and ICI, BP 446,910.

[101] Irving, Shaw, and ICI, BP 447,545.

[102] Ciba, BP 539,107.

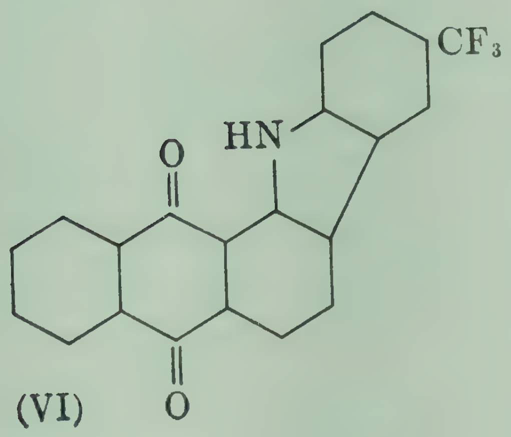
[103] IG, BP 458,099. See also Ciba, SP 257,722.

[104] IG, BP 439,180; Gubelmann, Goodrich, Dettwyler, and du Pont, USP 2,001,418–9. See also Max, Randall, and General Aniline and Film, BP 620,782.

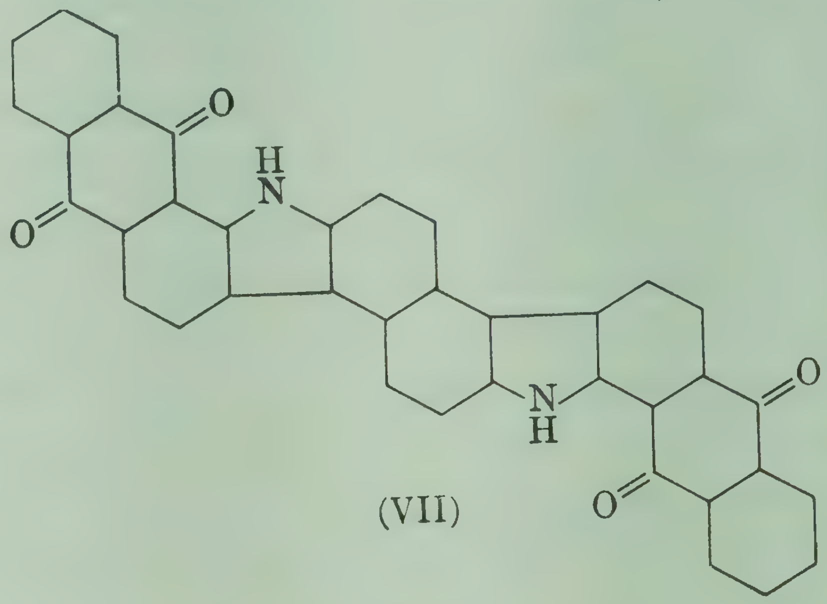
[105] Ciba, BP 381,942.

[106] Ciba, BP 381,920.

A carbazole derivative[109] with only one anthraquinone residue is the greenish yellow dye (VI), which is brighter and faster than the corresponding dye without the trifluoromethyl group, and which yields a useful leuco sulfuric ester. Carbazole vat dyes, derived from two anthraquinone molecules combined with one molecule of a naphthalene derivative such as 2,6-dibromonaphthalene, have been described;[110] the dyes (e.g. benzamido derivatives of VII) are red-brown to violet in shade. Using other polycyclic hydrocarbons, brown carbazole dyes have been obtained from compounds of the general type $(RNH)_nR'$, where $n = 1$ or more, R is a vattable residue, and R′ may be the radical of chrysene, phenanthrene, or fluoranthene.[111] 2,7-Dibromodiphenylene oxide and two moles of 1-amino-5-benzamidoanthraquinone, condensed and treated with sulfuric and nitrous acids, give a fast brown vat dye. Other vattable amines and the dibromo derivatives of thianthrene, diphenylene sulfide or sulfone, dinaphthylenethiophene, etc., may be used.[112]



(VI)



(VII)

IMIDAZOLE DERIVATIVES

When 2-amino-1,4-bisbenzamidoanthraquinone (I) is treated with concentrated sulfuric acid, cyclization to an imidazole occurs, together with hydrolysis of the 4-benzamido group; re-benzoylation of the 4-amino group is stated to yield a bright orange dye, Indanthrene Orange FFRK;[113] but the dye is not in the current IG shade card. Bisimidazole derivatives are obtained from *o*-amino alkyl- or arylaminoanthraquinones and the chlorides of aromatic *m*- or *p*-dicarboxylic acids.[114] The imidazoles from *o*-diaminoanthraquinones are sensitive to alkali, but the dialkyl or aryl derivatives (e.g. II) are fast yellow dyes. Useful dyes are obtained by condensing the imidazole from 3-bromo-1,2-diaminoanthraquinone (or a similar oxazole) with 1-amino-4- or 5-benzamidoanthraquinone.[115]

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[107] Ciba, BP 399,241.

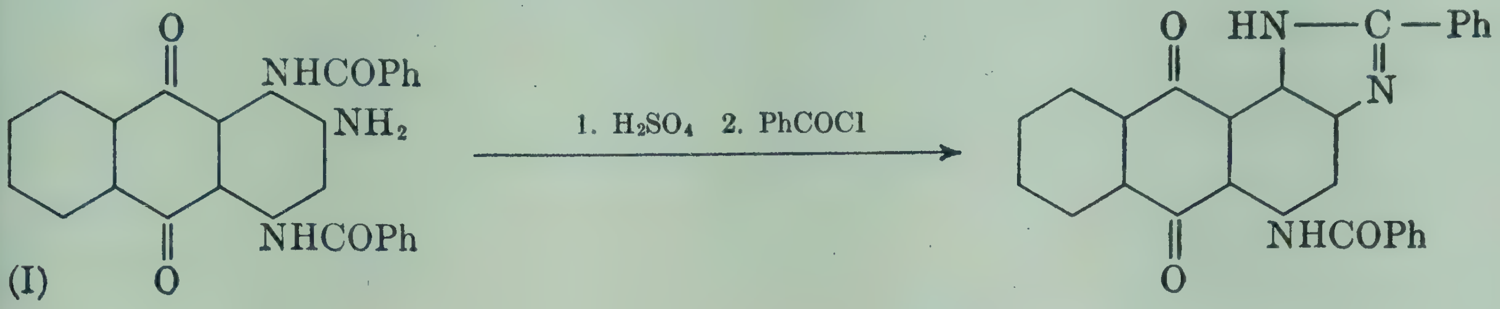
[108] Kuhlmann, FP 804,674.

[109] IG, BP 493,211.

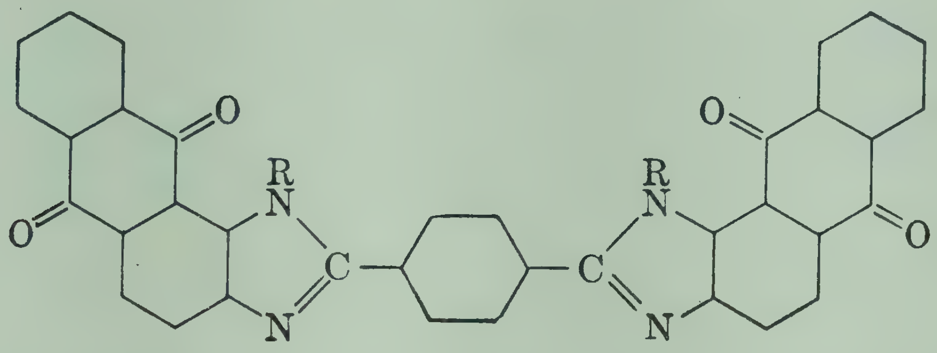
[110] Ciba, BP 522,657–8; SP 225,713.

[111] Ciba, BP 516,130–1; 519,776; 525,794; 636,205.

[112] Ciba, BP 542,577; SP 216,594–9; 218,368.



Indanthrene Orange FFRK



(II)

OXAZOLE DERIVATIVES

An oxazole derivative in the commercial range of anthraquinone vat dyes is Indanthrene Red FBB (Caledon Brilliant Red 3B) which gives a dull brown vat and dyes strawberry-red shades with very high all-round fastness (light 6–7; alkali boil 4–5; chlorine 5). Indanthrene Red FFB is apparently identical with Red FBB.[116] Like the analogous thiazoles, Indanthrene Blue CLG and Indanthrene Rubine B, Indanthrene Red FBB is interesting as being among the very few 2,3-substituted or linear derivatives of anthraquinone which have the requisite affinity for practical dyeing.

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[113] Rowe, The Development of the Chemistry of Commercial Dyes, Institute of Chemistry, London, 1938.

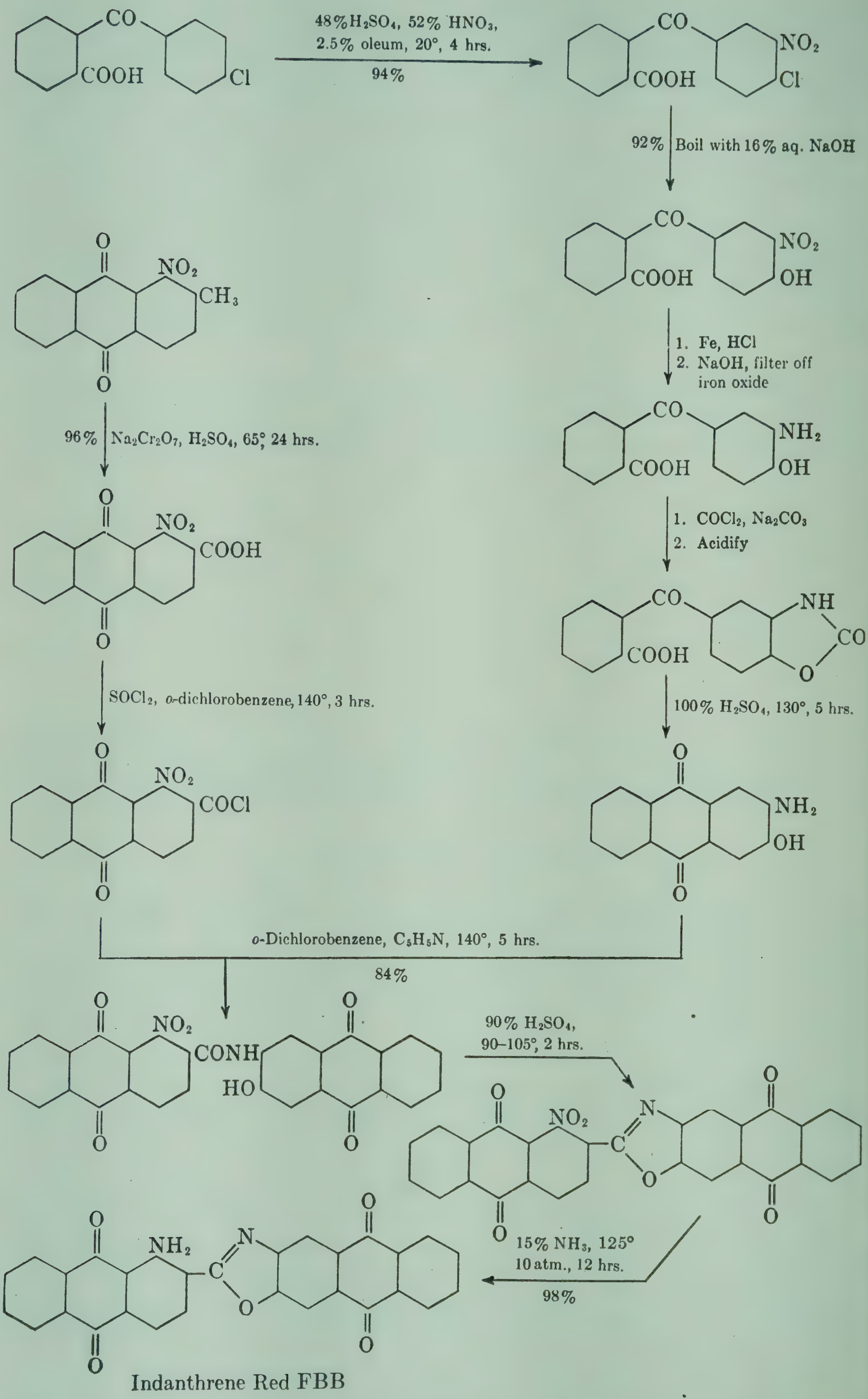
[114] IG, DRP Anm. J. 49,049.

[115] Kuhlmann, BP 591,980.

[116] Smith and Reid, *Chemistry & Industry* **43,** 675 (1948).

CHART 3

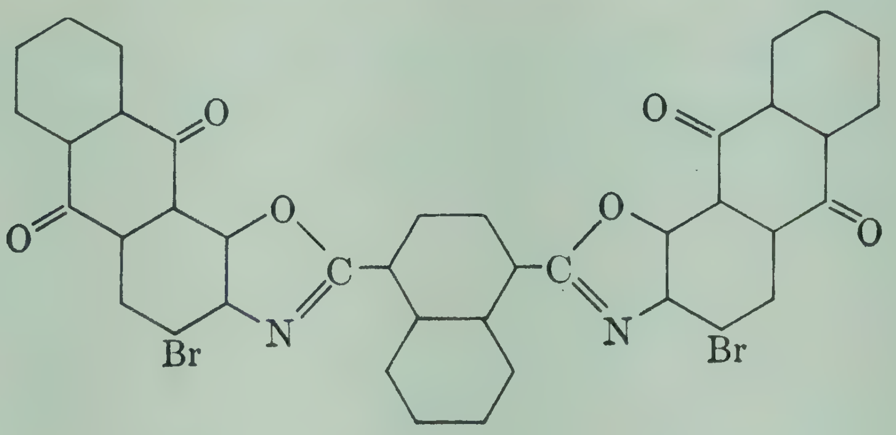
PREPARATION OF INDANTHRENE RED FBB

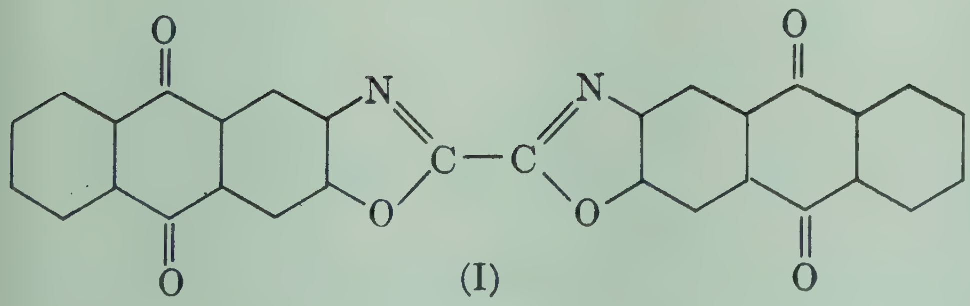

CO
COOH
Cl
48% H2SO4, 52% HNO3,
2.5% oleum, 20°, 4 hrs.
94%
CO
NO2
COOH
Cl
92%
Boil with 16% aq. NaOH
CO
NO2
COOH
OH
1. Fe, HCl
2. NaOH, filter off iron oxide
CO
NH2
COOH
OH
1. COCl2, Na2CO3
2. Acidify
CO
NH
CO
COOH
O
100% H2SO4, 130°, 5 hrs.
O
NH2
OH
O
O
NO2
CH3
O
96%
Na2Cr2O7, H2SO4, 65°, 24 hrs.
O
NO2
COOH
O
SOCl2, o-dichlorobenzene, 140°, 3 hrs.
O
NO2
COCl
O
o-Dichlorobenzene, C5H5N, 140°, 5 hrs.
84%
O
NO2
CONH
HO
O
O
O
90% H2SO4,
90–105°, 2 hrs.
O
NO2
N
C
O
O
O
O
15% NH3, 125°
10 atm., 12 hrs.
98%
O
NH2
N
C
O
O
O
O
Indanthrene Red FBB

Amino, acylamido, and cyano derivatives of Indanthrene Red FBB, which are blue, violet, gray, or brown dyestuffs, have been prepared.[117, 118] 2-Aminoquinizarin has been converted into bright red oxazole dyes by condensation with 1-aminoanthraquinone-2-carboxylic acid; the products may be alkylated.[119] 2,4-Bisacylamido-1-hydroxyanthraquinones have been used to form oxazoles by treatment with an acid condensing agent; yellow, orange, pink and brown vat dyes are obtained.[120] The simpler oxazoles have been used as dyestuff intermediates; 4-amino- or 4-halogeno-anthraquinone-1,2- or 2,1-oxazoles, condensed with halogeno- or aminoanthraquinones and cyclized to carbazoles, yield orange to red-brown dyes of excellent fastness.[121]

Yellow, brown and olive dyes have been prepared, in which the anthraquinone-oxazole is not attached to a nuclear carbon atom in the second anthraquinone residue, as in Indanthrene Red FBB, but by means of an imino or carboxylamido group.[122] Thus halogen derivatives of anthraquinone-oxazoles are condensed with aminoanthraquinones, giving red, blue and violet vat dyes.[123] Oxazoles, thiazoles or imidazoles, in which the carbon atom in the azole ring is unsubstituted, condense to bimolecular products on treatment with copper salts in solvents. With anthraquinone derivatives, the dyes (e.g. I) are apparently identical with the products of the interaction of 2-amino-3-hydroxy or 3-mercapto-

(II)





(I)

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[117] IG, BP 420,359.

[118] IG, FP 785,275; Ciba, BP 630,375.

[119] IG, DRP Anm. J. 54,601.

[120] IG, BP 454,237.

[121] IG, DRP Anm. J. 51,078.

[122] IG, BP 478,700.

[123] Kuhlmann, FP 854,356.

anthraquinone or 2,3-diaminoanthraquinone with oxalic acid or glyoxal.[124]

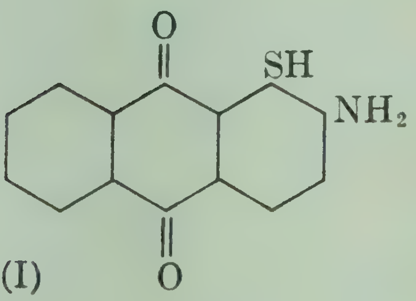
1-Bromo-2-aminoanthraquinones, on heating with an acid chloride, potassium acetate and a copper salt, undergo cyclization to oxazoles. Using 1,3-dibromo-2-aminoanthraquinone and naphthalene-1,4-dicarboxylic acid, the bis-oxazole (II) dyes cotton a fast, bright yellow.[125] Condensing (II) and its analogs with α-aminoanthraquinone, the bis-dianthrimides dye orange shades "exhibiting better light fastness than the existing orange dyes." Red vat dyes are obtained by cyclizing a 1,2-bis (anthraquinonylcarbonyl) hydrazine to the 2,5-dianthraquinonyl-1,3,4-oxadiazole.[125a]

Yellow anthraquinoneselenazole vat dyes have been prepared by condensing 2-amino-1-selenoloanthraquinones with aromatic mono- or dicarboxylic chlorides.[126]

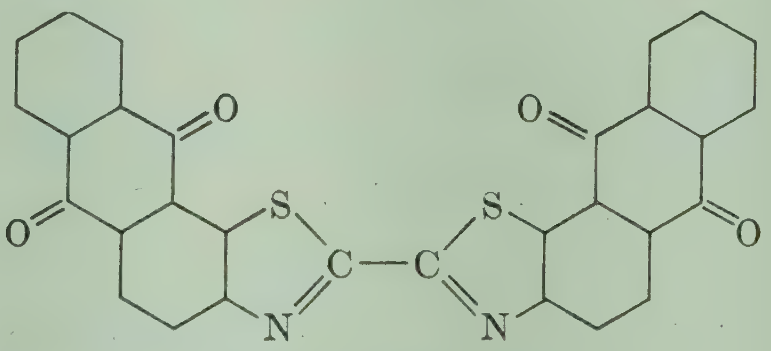
THIAZOLE DERIVATIVES

In view of the structural analogy with the pyrazole, imidazole and oxazole derivatives, it is convenient at this stage to deal with vat dyes prepared from anthraquinone-thiazoles: anthraquinonoid vat dyes containing the thiazole ring system also occur among the sulfurized vat dyes.[64]

Algol Yellow 8G, prepared by the action of glyoxal on 2-amino-1-mercaptoanthraquinone (I) in sulfuric acid solution followed by hypochlorite oxidation, is not marketed as such, since it is a tenderer and the light fastness is low for a vat dye, but it is used as a shading color, being useful for this purpose because of its ready applicability by all the vat dyeing methods.[2] Glyoxal, in the form of its sulfate, is made by the interaction of tetrachloroethane and 65% oleum in presence of a little mercuric chloride, and (I) is made by heating 1-chloro-2-aminoanthraquinone with sodium sulfide, sulfur and water.



(I)



Algol Yellow 8G

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[124] IG, BP 478,549.

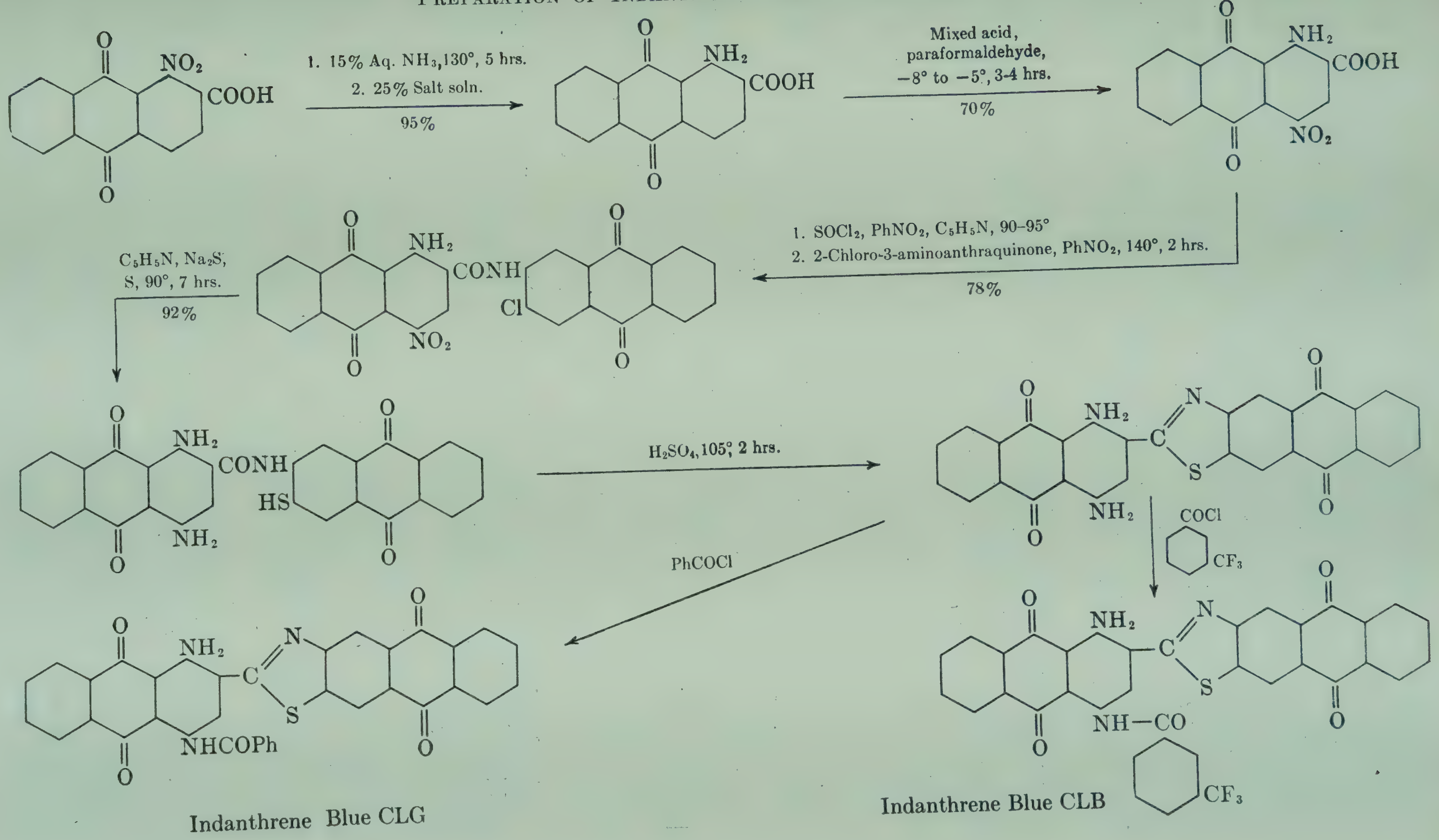
[125] Deinet and du Pont, USP 2,415,937–8.

[125a] Stilmar and du Pont, USP 2,464,831.

[126] du Pont, BP 423,447.

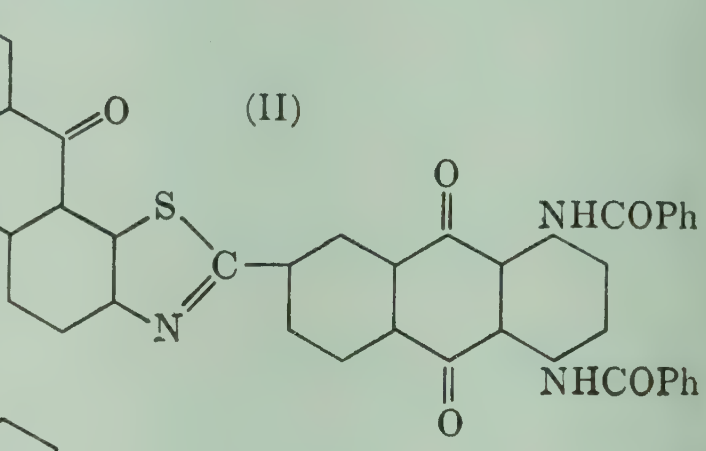
CHART 4

Preparation of Indanthrene Blue CLB and CLG

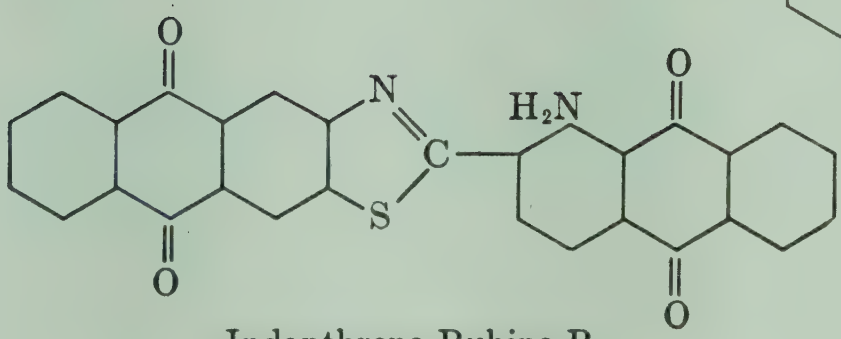

NO₂
COOH
1. 15% Aq. NH₃,130°, 5 hrs.
2. 25% Salt soln.
95%
NH₂
COOH
Mixed acid,
paraformaldehyde,
−8° to −5°, 3-4 hrs.
70%
NH₂
COOH
NO₂
1. SOCl₂, PhNO₂, C₅H₅N, 90–95°
2. 2-Chloro-3-aminoanthraquinone, PhNO₂, 140°, 2 hrs.
78%
NH₂
CONH
Cl
NO₂
C₅H₅N, Na₂S,
S, 90°, 7 hrs.
92%
NH₂
CONH
HS
NH₂
H₂SO₄, 105°, 2 hrs.
NH₂
C
N
S
NH₂
COCl
CF₃
PhCOCl
NH₂
C
N
S
NHCOPh
Indanthrene Blue CLG
NH₂
C
N
S
NH—CO
CF₃
Indanthrene Blue CLB
O

Indanthrene Rubine B, Blue CLG and Blue CLB are recent IG introductions, which are interesting as linear or 2,3-substituted anthraquinone derivatives, while the 1,2- or angular orientation is much more common. The preparation of Indanthrene Blue CLB is outlined in Chart 4, and Blue CLG is the analogous dye without the trifluoromethyl group. Indanthrene Blue CLB has excellent all-round fastness, and examples of other dyes containing the remarkably stable trifluoromethyl group,[127, 128] which is claimed to increase the brightness, tinctorial value, and light fastness, have been cited elsewhere; the fastness to chlorine (5) is noteworthy in view of the relatively low chlorine fastness of other vat blues.

Indanthrene Rubine B, which has a light fastness (6–7) a grade lower than Blue CLB, is prepared by a similar thiazole synthesis from the same intermediate, 2-chloro-3-aminoanthraquinone.

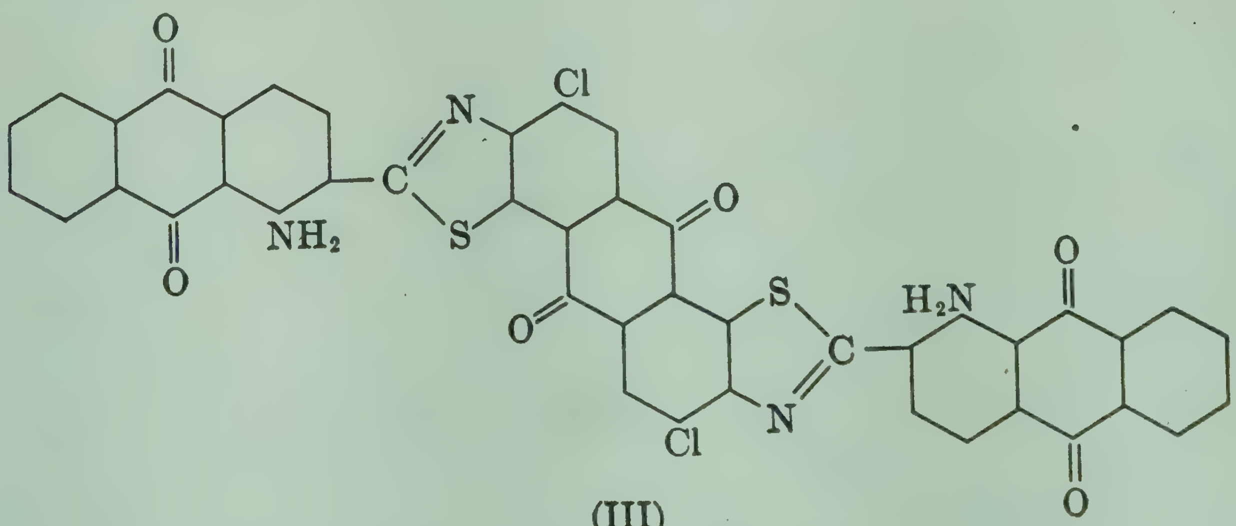


(II)



Indanthrene Rubine B

Condensing 2-amino-1-mercaptoanthraquinone with the chloride of 1,4-bisbenzamidoanthraquinone-6-carboxylic acid, the product (II) is a red-brown printing vat dye of good fastness.[129]



(III)

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[127] See also IG, BP 436,951; DRP 745,417; FP 825,573.

[128] IG, BP 480,749; 512,580.

[129] Graham and du Pont, USP 2,179,551.

An alternative route to these thiazoles is to condense an aminomercaptoanthraquinone with 1-aminoanthraquinone-2-aldehyde by means of 90–100% sulfuric acid; the azomethine first formed undergoes oxidation and cyclization to the thiazole. Anthraquinonedithiazoles (e.g. III), prepared in this manner from 3,7-dichloro-2,6-diamino-1,5-dimercaptoanthraquinone and two moles of 1-aminoanthraquinone-2-aldehyde, are vat dyes of excellent fastness.[130]

ACRIDONES

Anthraquinone vat dyes containing the acridone ring system were first made by Ullmann in 1909, and although many acridones derived from anthraquinone have been synthesized, CI records only three dyes of this type. More recently there has been considerable activity in this field as shown by the patent literature. The anthraquinone vat dye range now includes nearly twenty acridones, which have excellent fastness to light and chlorine, but the fastness to alkali boil is of a lower degree, and the use of the dyes is therefore limited mainly to piece dyeing. The average fastness grades of acridones are: light 7, chlorine 4, and soda boil 3. The acridone dyes are generally of the cold dyeing class, giving readily soluble vats with good substantivity. The shades of the commercial dyes now cover a very wide range including orange, red, violet, blue, green, brown and khaki. The deeper shades and the tertiary shades are produced by the addition of other heterocyclic systems such as quinazoline and carbazole and the alkali fastness is simultaneously improved. The alkali-hydrosulfite vats are usually brown, wine-red or violet in color.

Of the three isomeric anthraquinone-acridones, it is only the α-aminoanthraquinone derivatives (I) which are technically important. The parent compound (I) is red-violet, and the introduction of an amino group in the 6-position gives a blue dye. Two variations of the type (I) are to be found among the technically useful dyes. While the pyridone ring in (I) unites an anthraquinone nucleus with a benzene ring, the latter may be replaced by naphthalene or anthraquinone. Secondly, two acridone systems may be present in conjunction with one anthraquinone nucleus.

Synthetic routes. The main synthetic method consists in the cyclization of a 1-arylaminoanthraquinone carboxylic acid, in which the carboxyl group is adjacent to the imino group in the anthraquinone nucleus as in (II) or in the aryl residue as in (III). The cyclization is usually effected

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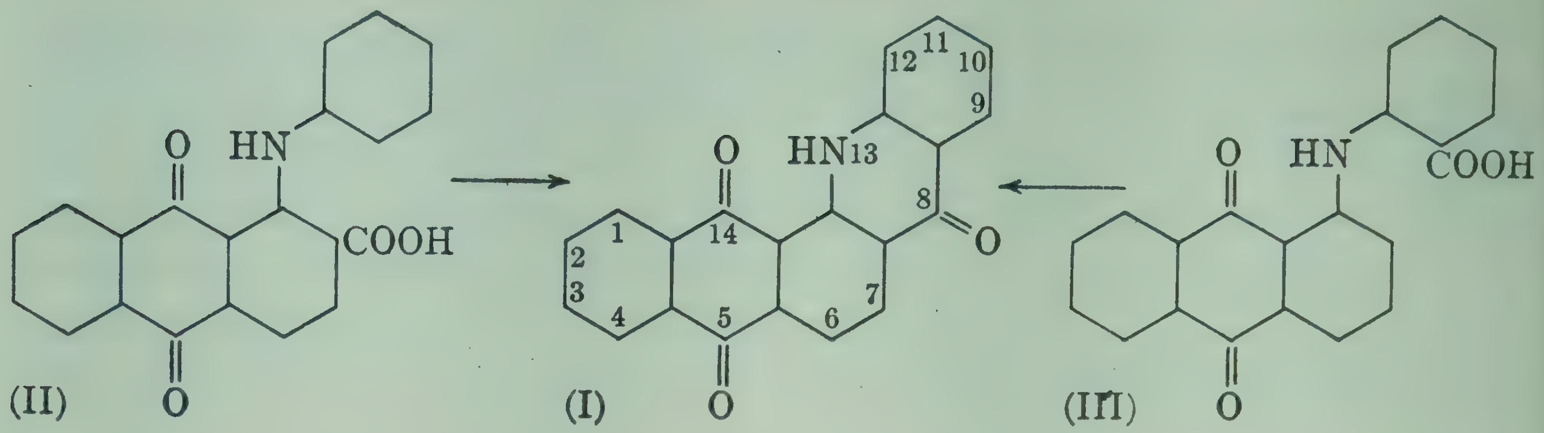
[130] Rintelman and du Pont, USP 2,335,698.



by means of concentrated sulfuric acid at about 100°.[131] Chlorosulfonic acid may be added, or used by itself,[132] and among other cyclizing agents are acetic anhydride and acetyl chloride, ferric chloride, benzoyl chloride,[133] phosphorus pentachloride and thionyl chloride.[134] The action of aluminum chloride on the chloride of (II) or (III),[135] and of zinc dust and ammonia or of sodium hydrosulfite on their esters, are other methods for the preparation of (I).[136]

The acids (II) and (III) are usually prepared by an application of the Ullmann reaction in which the condensation may be between 1-chloroanthraquinone-2-carboxylic acid and aniline, or 1-chloroanthraquinone and anthranilic acid, or 1-aminoanthraquinone and *o*-chlorobenzoic acid.[131] The preferred method depends on the accessibility of the intermediates for the various types of acridone dyes. When one of the reactants is an anthraquinone carboxylic acid, the use of sodium acetate as an acid-binding agent in the Ullmann synthesis leads to some decarboxylation and low yields; better yields are obtained by using a carbonate, e.g. of calcium or magnesium.[137] Another useful method for the preparation of 1-arylaminoanthraquinone carboxylic acids is the condensation of 1-nitroanthraquinone-2-carboxylic acid with an aromatic amine or of a nitroanthraquinone with an arylamine-*o*-carboxylic acid; under suitable conditions, e.g. by using arsenic or phosphorus chloride (cf. preparation of Indanthrene Red RK), the reaction proceeds directly to the acridone. 1-Nitroanthraquinone-2-carboxylic acid is an important intermediate for the acridone dyes. Some of the other routes to the penultimate intermediates represented by (II) and (III) are the oxidation or alkali fusion of 1-arylamino-2-methylanthraquinone or its chlorination to the trichloromethyl compound, followed by hydrolysis to the carboxylic acid or chloride;[138, 139] the hydrolysis of 1-arylamino-2-cyanoanthraquinone; and the addition of 1-aminoanthraquinone to 1,2-naphthoquinone-3-carboxylic acid with the formation of (IV).

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[131] Ullmann and Ochsner, *Ann.* **381,** 1 (1911); Ullmann and Eiser, *Ber.* **49,** 2154 (1916); Ullmann and Dootson, *ibid.* **51,** 9 (1918); Ullmann, DRP 221,853; BASF, DRP 237,546; 240,002; MLB, DRP 240,327; BASF, DRP 269,850.

[132] MLB, DRP 243,586; IG, DRP 531,013.

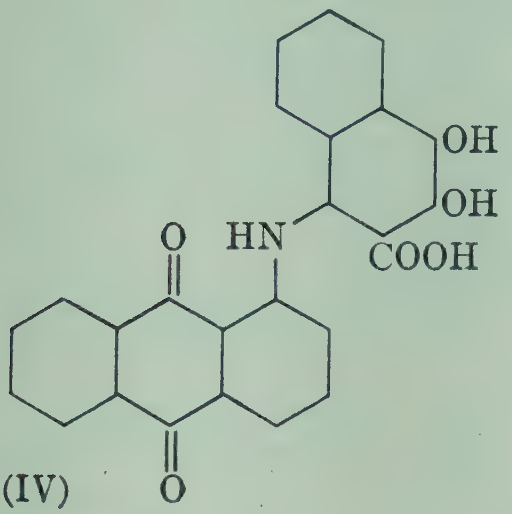
[133] BASF, DRP 248,170; Bauer, Hoyer, Bollweg, and General Aniline Works, USP 2,097,112.

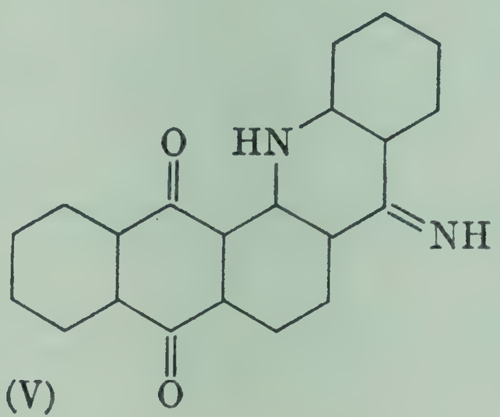
[134] Ullmann and Sone, *Ann.* **380,** 336 (1911); Ullmann and Billig, *ibid.* **381,** 22 (1911); BASF, DRP 237,236–7; USP 1,967,364.

[135] Ullmann, *Ber.* **43,** 536 (1910); Ullmann and Dasgupta, *ibid.* **47,** 553 (1914).

[136] BASF, DRP 246,966.

[137] BASF, DRP 268,219.


(IV)


(V)

Methods have also been described in which the acridone synthesis does not proceed through carboxylic acids such as (II) and (III). The cyclization of an arylaminocyanoanthraquinone to an acridone may proceed through the formation of the ketimide (V), rather than the carboxylic acid (II or III).[139, 140] More interesting is the action of aluminum chloride in nitrobenzene on the anthraquinonyl-isatin (VI), when carbon monoxide is lost and the acridone (I) is formed; (VI) results from the condensation of 1-chloroanthraquinone and isatin or 1-anilinoanthraquinone and oxalyl chloride.[141] A method in which a 2-benzoylanthraquinone is converted into an acridone by effecting the necessary imino linkage, in contrast to the normal procedure of cyclizing an arylaminoanthraquinone carboxylic acid, is to heat 1-chloro-2-*o*-chlorobenzoylanthraquinone with *p*-toluenesulfonamide.[142] 1-Aminoanthraquinone-2-aldehyde and β-naphthol condense in presence of sulfuric or phosphoric acid to form 3,4-phthaloyl-7,8-benzacridine (VII), oxidizable to a red vat dye.[142a]

Shades of the acridone dyes. The parent acridone (I), conveniently prepared from 1-chloroanthraquinone-2-carboxylic acid (VIII) and aniline, is not useful as a dye; but when 1-anilinoanthraquinone-2-carboxylic acid (II) is chlorinated in sulfuric acid solution, cyclization

---

[138] BASF, DRP 192,436; 272,296; 275,671; 283,724.

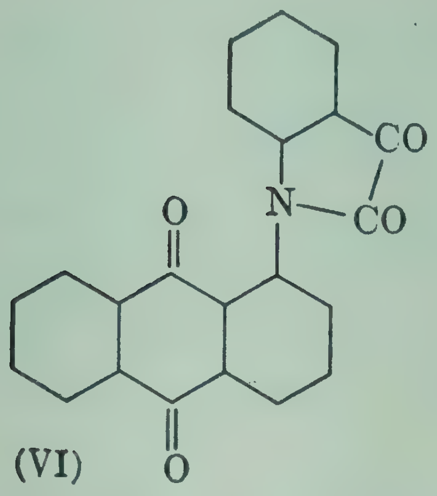
[139] Schaarschmidt, *Ann.* **405**, 95 (1914).

[140] Schaarschmidt, DRP 269,800.

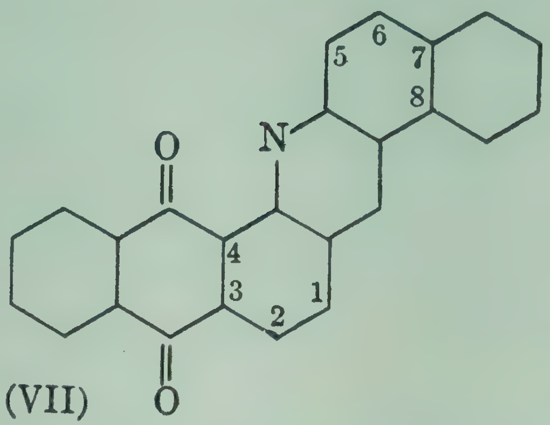
[141] Bayer, DRP 286,095.

[142] BASF, DRP 272,297.

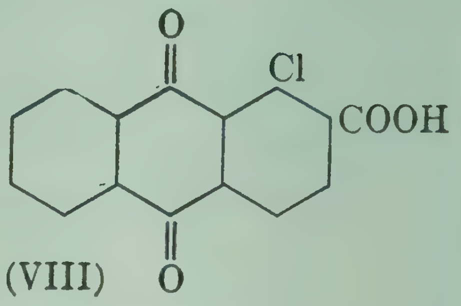
[142a] IG, BP 508,708.



(VI)



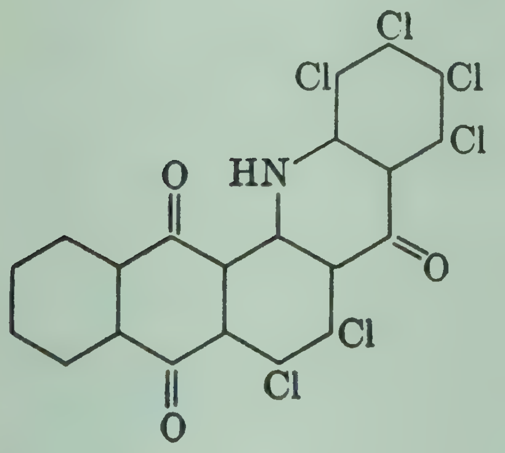
(VII)



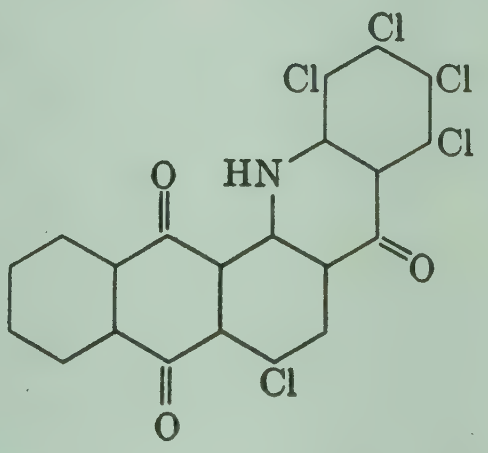
(VIII)

and halogenation take place simultaneously, and the trichloro compound was marketed as Indanthrene Red Violet RRK (Bally, 1910) (BASF; CI, 1161) (Caledon Red Violet 2RN).[17, 143] The acridone (I) may be isolated and chlorinated subsequently, e.g. by means of sulfuryl chloride. Maki and Eguchi[144] have prepared pure mono-, di- and trichloro derivatives of (I) by progressive chlorination with sulfuryl chloride in presence of iodine, and from the color reactions and analysis they conclude that Indanthrene Red Violet RRK consists of 78% trichloro and 22% dichloro compounds. They have assumed that the trichlorination takes place entirely in the benzene ring. Indanthrene Red Violet RRK has also been stated to be the 6,10,12–trichloro derivative of (I).[24] The profound influence of the number and position of the chlorine atoms is shown by the following examples of the color of chloro derivatives of (I): 12-chloro, bluish-red; 9,12-dichloro, claret red; 9,11-dichloro, orange; 10,12-dichloro, violet; 9,10,12-trichloro, claret red; 9,11,12-trichloro, orange.

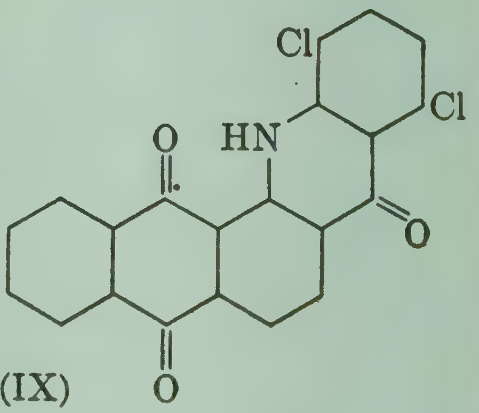
Caledon Red Violet 2RN and Tinon Chlorine Red Violet 2RN appear to be chlorinated acridones analogous to Indanthrene Red Violet RRK.[144a] Pentachloro and hexachloro derivatives of (I) have



Indanthrene Pink B



Indanthrene Brilliant Pink BBL



(IX)

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[143] BASF, DRP 258,561; DRP 522,969; 529,555; Rowe ascribes this constitution to Indanthrene Red Violet RRN which is a thioindigoid dye.

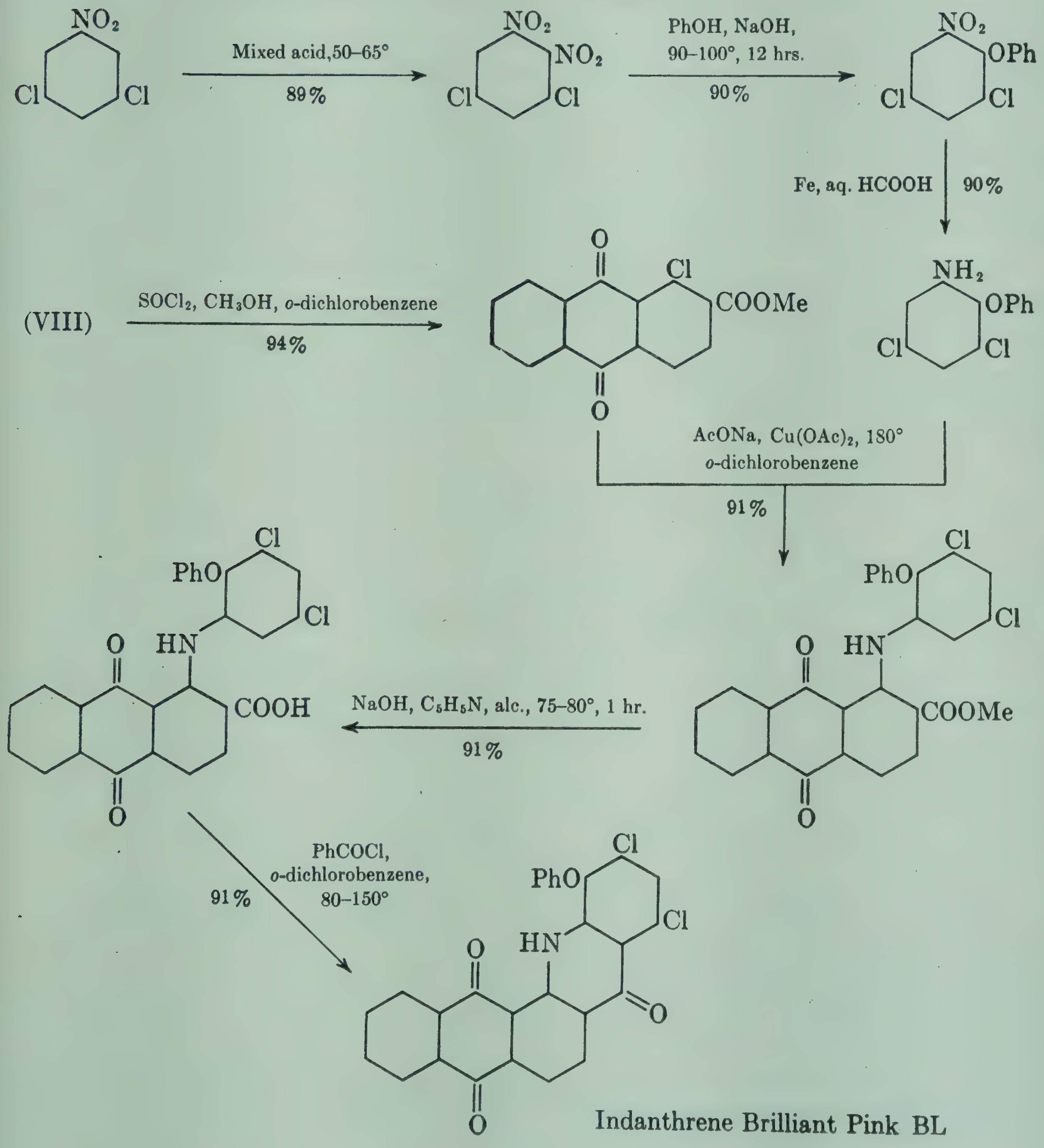
[144] *Soc. Chem. Ind. Japan*, **44**, 788 (1941).

[144a] According to Fox, *J. Soc. Dyers Colourists* **65**, 515 (1949), Caledon Red Violet 2RN is mainly the 9,10,11-trichloro derivative of (I).

also been marketed. When 1-nitro-2-methylanthraquinone is condensed with aniline at 175°, and the 1-anilino-2-methylanthraquinone thus formed is treated with chlorine in nitrobenzene or trichlorobenzene solution, the product is the hexachloro derivative of (I), Indanthrene Pink B. One of the chlorine atoms (probably the 7-substituent) is labile, and is removed under the ordinary conditions of vatting with hydrosulfite and caustic soda; the hexachloro compound has therefore become obsolete, and the pentachloro compound is marketed as Indanthrene Brilliant Pink BBL. The dye appears to have been sold formerly under the name Indanthrene Pink FBBL, and it will probably be withdrawn

CHART 5

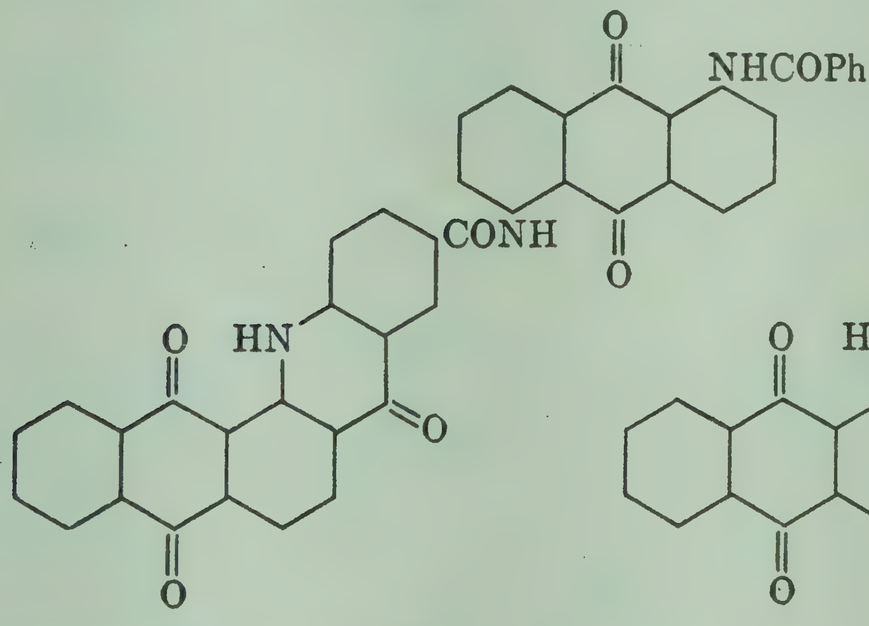
Preparation of Indanthrene Brilliant Pink BL


NO₂
Cl
Cl
Mixed acid,50–65°
89%
NO₂
NO₂
Cl
Cl
PhOH, NaOH,
90–100°, 12 hrs.
90%
NO₂
OPh
Cl
Cl
Fe, aq. HCOOH
90%
(VIII)
SOCl₂, CH₃OH, o-dichlorobenzene
94%
O
Cl
COOMe
O
NH₂
OPh
Cl
Cl
AcONa, Cu(OAc)₂, 180°
o-dichlorobenzene
91%
Cl
PhO
Cl
O
HN
COOH
O
NaOH, C₅H₅N, alc., 75–80°, 1 hr.
91%
Cl
PhO
Cl
O
HN
COOMe
O
PhCOCl,
o-dichlorobenzene,
80–150°
91%
Cl
PhO
Cl
O
HN
O
O
Indanthrene Brilliant Pink BL

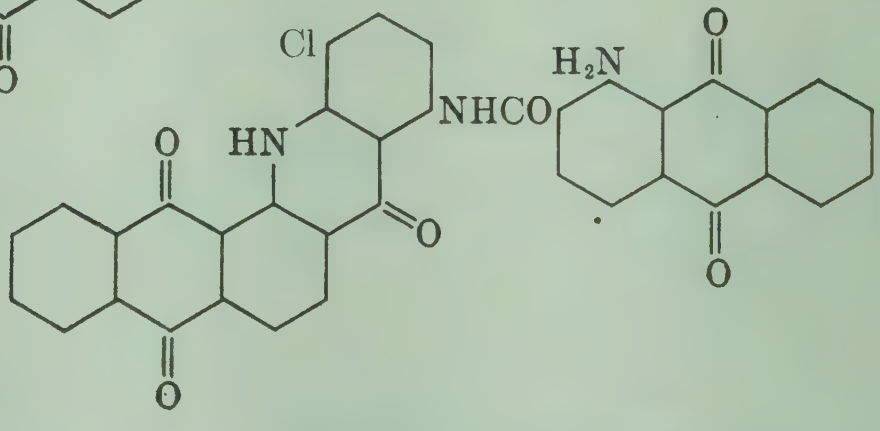
from the selling range.[2] These violet and pink chloroacridones have maximum light fastness (8), but the fastness to alkali boil is low (2), and they are only recommended for piece dyeing. When a halogen is in the 7-position and two halogen atoms (of which one is in the 9- or 11-position) are in the benzene ring, the tinctorial power is increased; thus the 7,9,10,-11,12-pentachloro compound is an intense and brilliant red vat dye.[145] The di- or trichloro derivatives of (I), made by condensing 1-chloroanthraquinone-2-carboxylic acid (VIII) with 2,5-dichloro- or a trichloroaniline and further cyclization of the intermediate carboxylic acid, are orange to red dyes which are claimed to be fast to caustic alkali boiling; e.g. (IX).[146]

The red to violet dyes obtained by cyclizing 1-(2′-phenoxy)anilinoanthraquinone-2-carboxylic acid have good fastness to light and boiling.[147] The introduction of two chlorine atoms in a dye of this type leads to a pink dye (Indanthrene Brilliant Pink BL), which is prepared by the indicated series of reactions;[4, 148] the dye has better fastness to light than Indanthrene Brilliant Pink R,[149] and has the further advantage over the latter dye of being nontendering. Indanthrene Brilliant Pink BL is stated to be specially valuable for furnishing fabrics.

Derivatives of (I) having a carboxyl group in the benzene ring, which may be used to acylate aminoanthraquinones, are obtained by condensing 1-chloroanthraquinone-2-carboxylic acid with an aminoarylcarboxylic acid and then cyclizing.[150] Indanthrene Orange RR, which has excellent all-round fastness (light 7–8; chlorine 5; soda boil 4) and is free from the



Indanthrene Orange RR



Indanthrene Bordeaux BB

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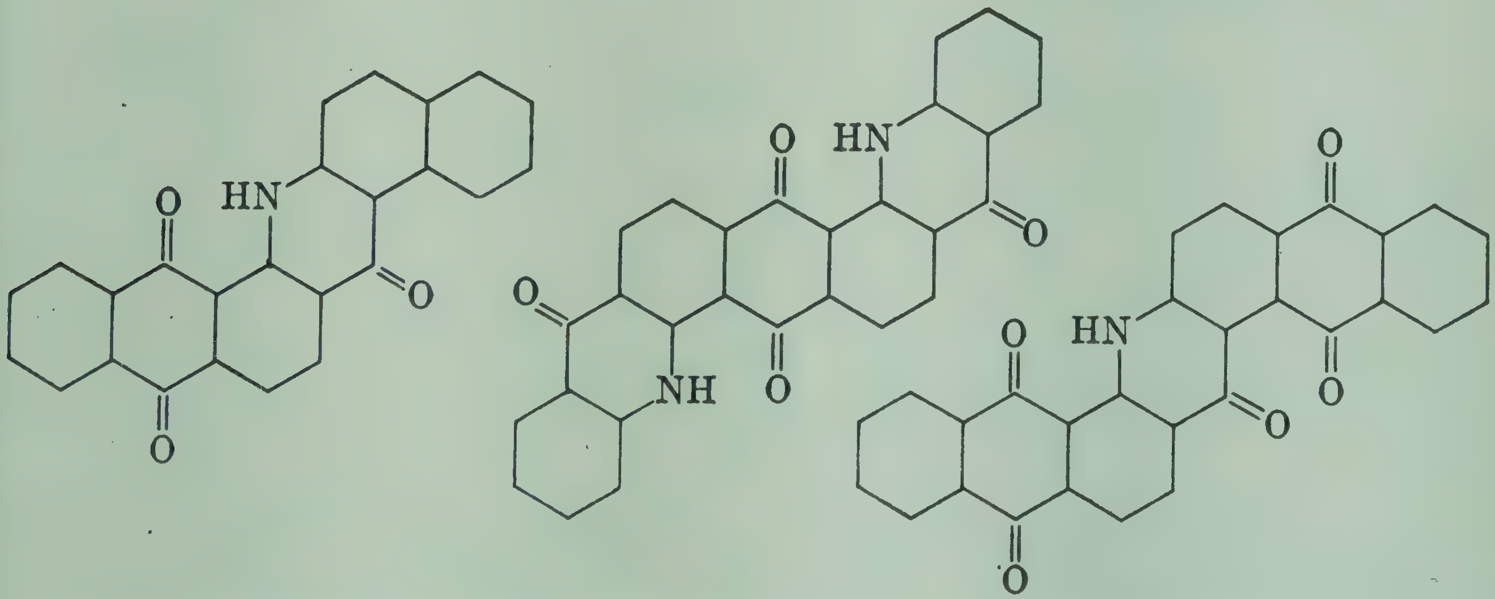
[145] IG, BP 399,491; DRP 582,169.
[146] IG, BP 366,055.
[147] IG, BP 458,166.
[148] *BIOS* **1088.**
[149] See Chapter XXXIII.
[150] Wuertz and du Pont, USP 1,950,348.

tendering defect, is prepared by condensing 1-nitroanthraquinone-2-carboxylic acid with *p*-aminobenzoic acid in aqueous solution in presence of magnesium oxide, cyclizing to the acridone, converting the 10-carboxyl group to the chloride by means of thionyl chloride, and finally condensing the acid chloride with 1-amino-5-benzamidoanthraquinone. In view of manufacturing difficulties IG had not planned to produce the dye on a technical scale.[2]

By linking up an acridone of the type of (I) with α-aminoanthraquinone through an —NHCO— group, a bordeaux dye (Indanthrene Bordeaux BB) is produced.[2]

A naphthalene analog of (I), prepared in one operation by heating 1-nitroanthraquinone-2-carboxylic acid, β-naphthylamine (2 moles) and arsenic trichloride (or trioxide) in *o*-dichlorobenzene, is Indanthrene Red RK (BN, BASF; CI 1162). It is curious that, while this β-naphthylamine derivative has been known and used for a long time (Lüttringhaus, 1910), the isomer from α-naphthylamine was described many years later (1937) as the basis of a series of bordeaux, violet, brown, olive-green, and gray dyes produced by suitable substitution.[151] Green, olive and brown shades are obtained by treating an *o*-carboxyanthraquinonylaminopyrene with an acid halide, and by nitration, halogenation, etc.[152]

The condensation of 1,5-dichloroanthraquinone with potassium anthranilate and cyclization by means of sulfuric acid or chlorosulfonic acid gives the bisacridone, Indanthrene Violet BN (RN, BASF; CI 1163) (Ullmann, 1909); a purer brand is marketed as Indanthrene Violet FFBN.



Indanthrene Red RK Indanthrene Violet RN Indanthrene Orange F3R

A bright orange dye in which two anthraquinone molecules are bridged by a pyridone ring is Indanthrene Orange F3R, which is the only one of the commercial acridones with the highest fastness to alkali boil (5). It is prepared by the interaction of 1-nitroanthraquinone-2-carboxylic acid and β-aminoanthraquinone in boiling *o*-dichlorobenzene in presence of sodium carbonate and cyclization with sulfuric acid.[153] An earlier brand of Indanthrene Orange F3R appears to have been a homolog of the indicated structure; one of the anthraquinone units contained a methyl group, and the preparation was through a series of reactions starting from the condensation of phthalic anhydride and toluene.[18, 154] Red-brown, blue-green and gray dyes are obtained by the double cyclization of the condensation products of an *o*-chloroanthraquinone-carboxylic acid and a 2-(3′-aminobenzoyl)benzoic acid with suitable substituents in the 4′-position.[155] Benzamido derivatives of an isomer of Indanthrene Orange F3R, prepared for instance by the cyclization of 5-benzamido-1,1′-dianthrimide-2′-carboxylic acid, have been described.[156]

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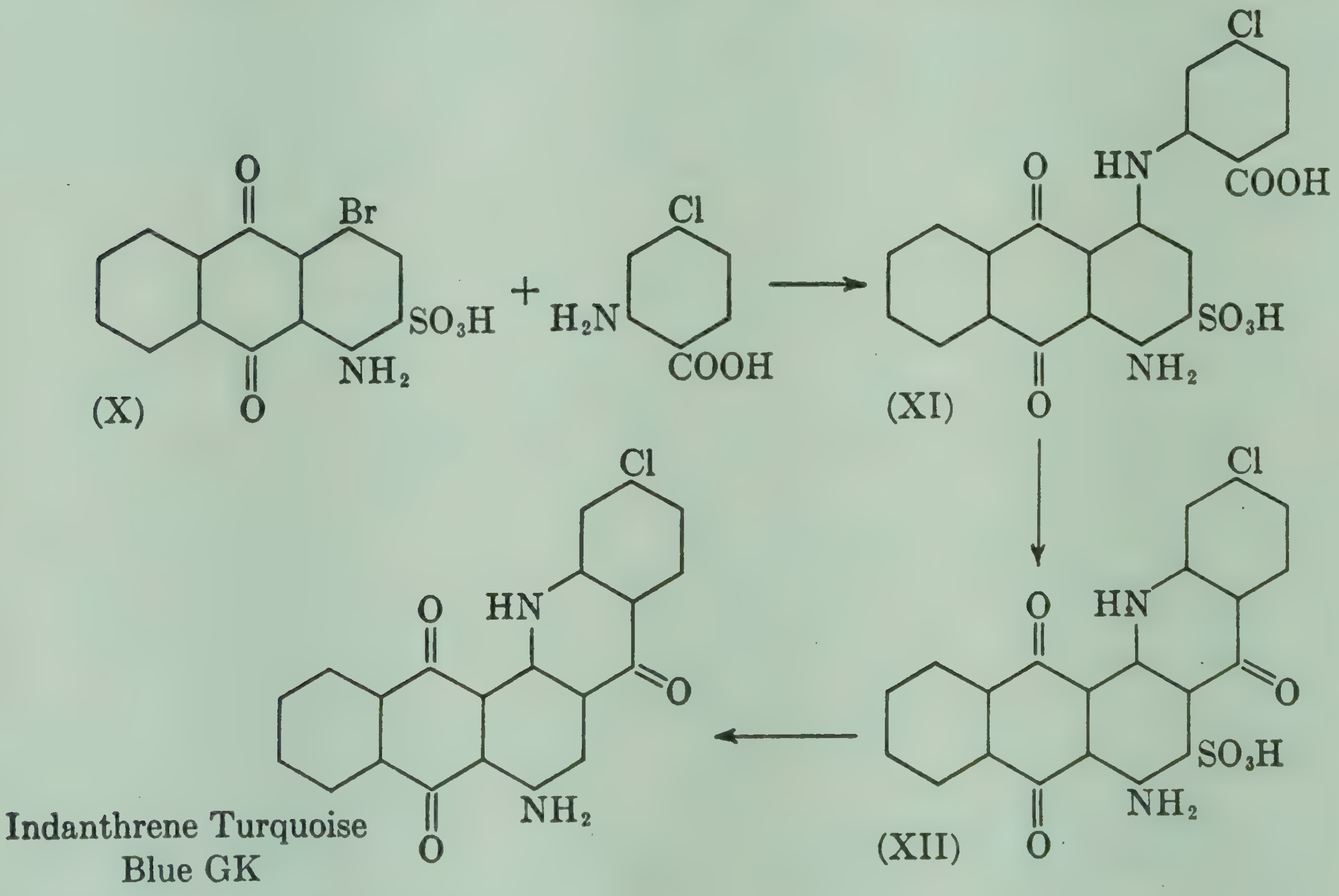
[151] Ciba, BP Appl. 797/1937.

[152] Ciba, BP 504,562; BP 525,795.

An important modification of the simple type represented by (I) and Indanthrene Red Violet RRK is the introduction of an amino group in the 6-position. Two valuable blue dyes, Indanthrene Turquoise Blue GK and 3GK, have been obtained in this manner, and a notable feature of the synthesis is the use of 4-bromo-1-aminoanthraquinone-2-sulfonic



(X)

(XI)

(XII)

Indanthrene Turquoise Blue GK

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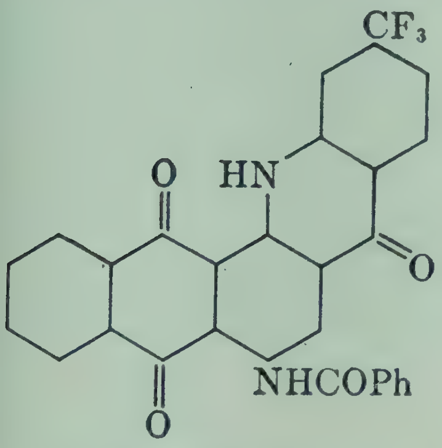
[153] See also BASF, DRP 279,867.

[154] BASF, DRP 237,546; 268,219.

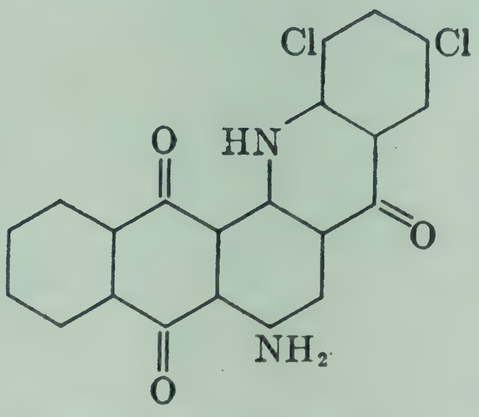
[155] ICI, BP 358,421.

[156] American Cyanamid, BP 592,970; 593,655; USP 2,449,011; 2,468,605; 2,492,802. See also USP 2,463,810; 2,475,521.

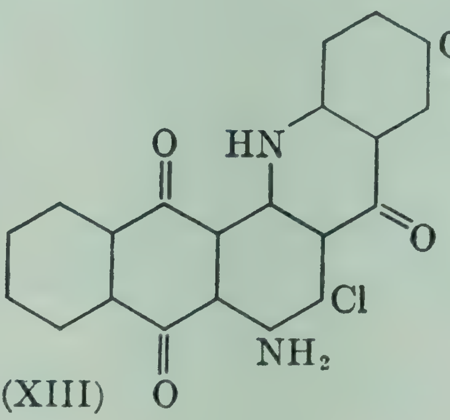
acid (X), which is produced on a large scale as an intermediate for a series of important acid anthraquinone dyes;[157] the anilinoanthraquinone preparation can thus be carried out in aqueous solution. After cyclization of (XI) to the acridone (XII), treatment with hydrosulfite and caustic soda solution[158] at about 60° removes the sulfonic group; in some cases (e.g., the condensation product of X and 4-trifluoromethylanthranilic acid), heating with sulfuric acid effects both ring closure and hydrolysis of the sulfonic group.[159] The dye obtained by benzoylation of the aminotrifluoromethyl derivative of (I) is an addition to the vat blues which IG were planning to introduce under the name Indanthrene Printing Blue FG.[4, 148, 160] The dye appeared to have a future in calico printing for its similarity in shade to Indanthrene Blue RSN, good dischargeability and improved fastness to chlorine. Indanthrene Turquoise Blue 3GK, which is made from (X) and 3,5-dichloroanthranilic acid,[161] has better fastness to soda boil than GK (4 against 2–3). Indanthrene Blue 8GK has been stated to have structure (XIII).[17, 162] Indanthrene Turquoise Blue 3GK is a greener blue than (XIII) (ST Erg II, p. 204); (XIII) can be synthesized by condensing 2,4-dichloro-1-aminoanthraquinone with 5-chloroanthranilic acid and cyclizing with concentrated sulfuric acid.[161] Although chlorine atoms in the β-positions in anthraquinone are generally much less readily removable by reduction than in α-positions, chlorine or bromine in the 7-position in acridones of the type



Indanthrene Printing
Blue FG



Indanthrene Turquoise
Blue 3GK



(XIII)

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[157] See Chapter XXIX.

[158] Neresheimer, USP 1,207,981; Allied Chemical and Dyestuff, USP 2,321,767, suggest the use of furfuraldehyde.

[159] IG, BP 495,375.

[160] See also IG, FP 837,183; USP 2,204,232.

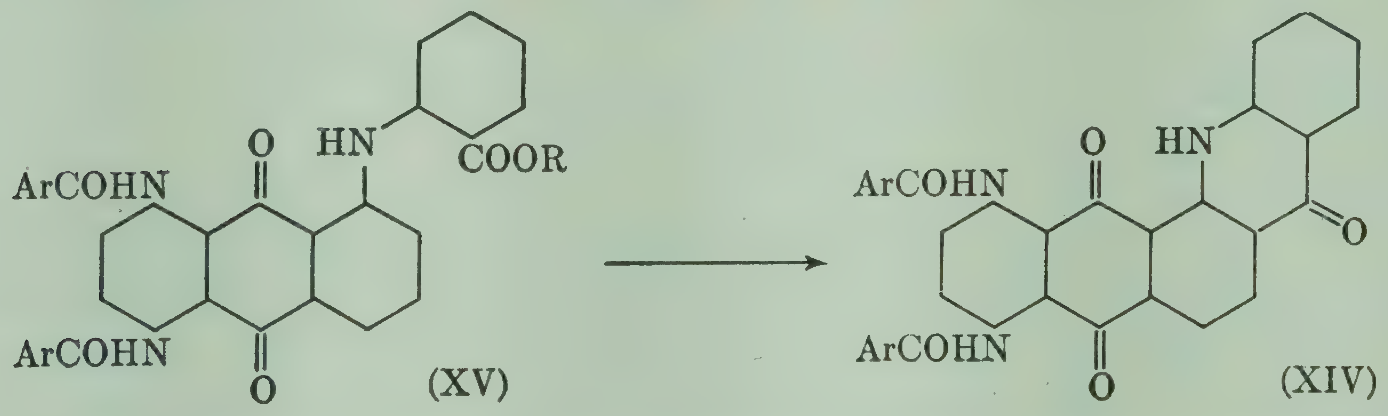
[161] Joshi, Tilak, and Venkataraman, *Proc. Indian Acad. Sci.* **32A,** 201 (1950). 2,4-Dichloro-1-aminoanthraquinone, useful as an intermediate for anthraquinonoid acid and vat dyes, can be prepared by chlorination of α-aminoanthraquinone in glacial acetic acid; Bedekar and Venkataraman, BP 634,645–6.

[162] IG, DRP 531,013; see *Friedländer* **20,** 1272 (1933).

of (XIII) is removed during vatting, so that such dyes have no practical value.[161] In fact, dyes of this series not containing halogen in the 7-position can be conveniently prepared by the condensation of 2-chloro-4-bromo-1-aminoanthraquinone with an anthranilic acid, cyclization, treatment with alkaline hydrosulfite and oxidation.[163]

Improved fastness to boiling alkali is obtained when a halogen atom is introduced into position 9, apparently because of its ability to inhibit the enolization of the adjacent carbonyl group.[164]

The *p*-chlorobenzoyl derivative of Indanthrene Turquoise Blue GK is also a blue dye.[164a] 6-Amino or 6-benzamido derivatives of (I), containing an SO_2Alk or SO_2Ar group in the benzene ring of the acyl or acridone group, are level-dyeing blue or violet dyes with excellent light fastness.[165] The 6-cinnamoylamido derivative of (I) has excellent fastness.[165a] Dyes containing an acylamido group in position 6 and chlorine in 9, 11, 12 are blue, and have good levelling properties on cotton and viscose. If there are benzamido groups in the 1,4-positions and halogen in 12, blue dyes fast to chlorine are obtained.[166] Dyes of the type (XIV) can be prepared by condensing a 5-amino- or 5-halogeno-1,4-bisaroylamidoanthraquinone with an *o*-halogeno- or aminobenzoic acid or ester, and cyclizing the product (XV). To avoid hydrolysis of the aroyl groups the cyclization has to be carried out under very mild conditions and is effected preferably by vatting the intermediate ester with alkaline hydrosulfite.[167]



(XV) (XIV)

The only homogeneous green dyes in the commercial range of anthraquinone vat dyes available until recently were bluish in tone, and a purer or more yellowish green could only be produced by admixture with a

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[163] Lodge and ICI, BP 587,006.

[164] IG, BP 491,525. See also *Annual Repts. Soc. Chem. Ind. London* **24,** 126 (1939).

[164a] General Aniline and Film, BP 633,132.

[165] Heslop, Irving, Livingston and ICI, BP 586,999; 587,010; USP 2,470,032; 2,481,744.

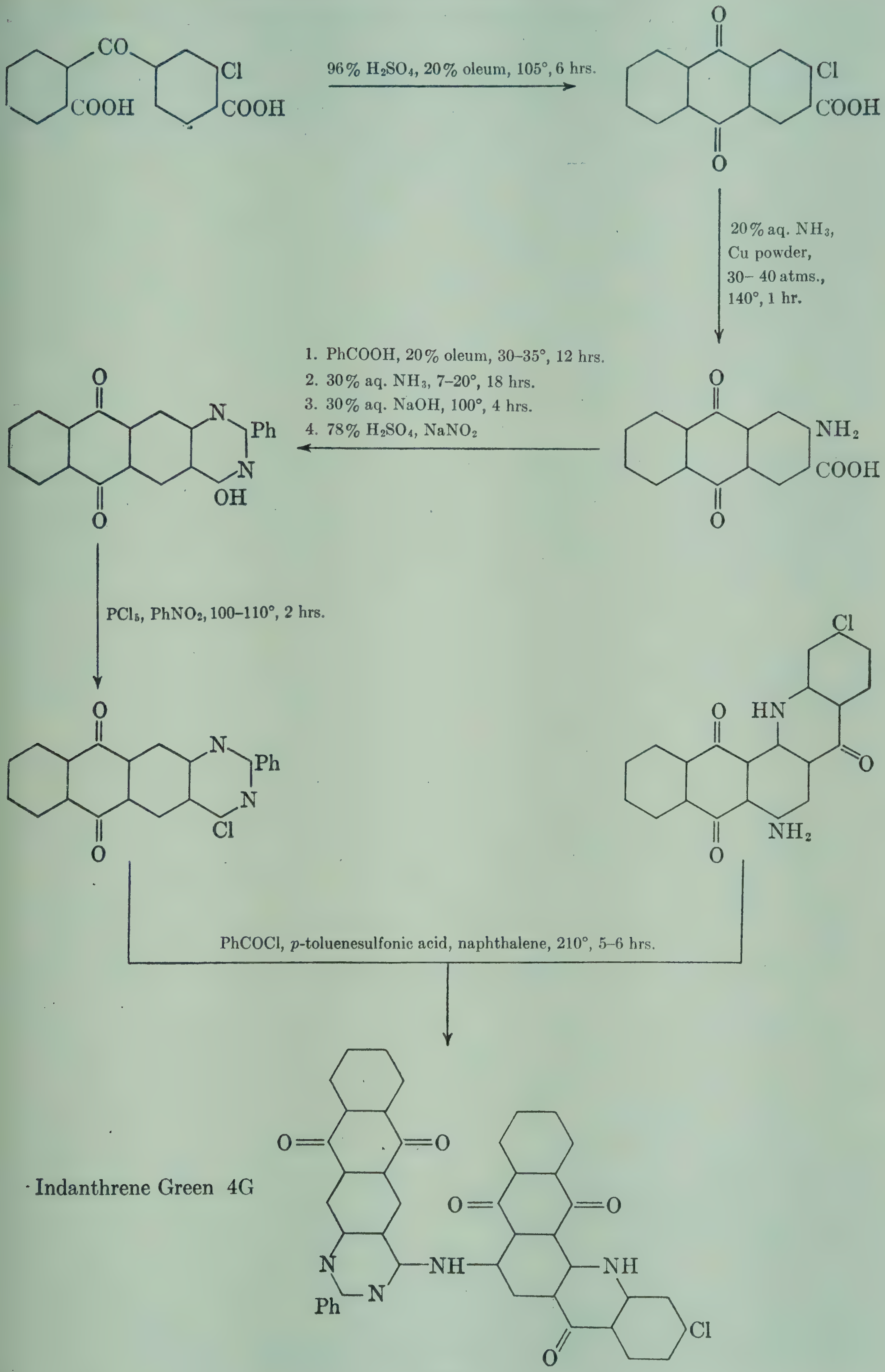
[165a] Ciba, USP 2,466,960. See also Sandoz, SP 258,766–7.

[166] IG, DRP Anm. J. 44,742; IG, BP 399,182; see also Ciba, BP 592,268; 593,804; 604,981.

[167] IG, BP 421,591.

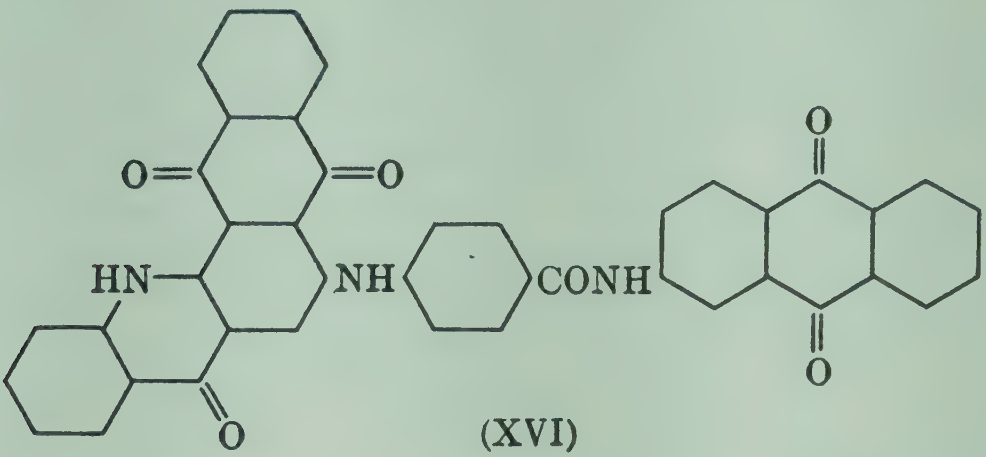
CHART 6

PREPARATION OF INDANTHRENE GREEN 4G

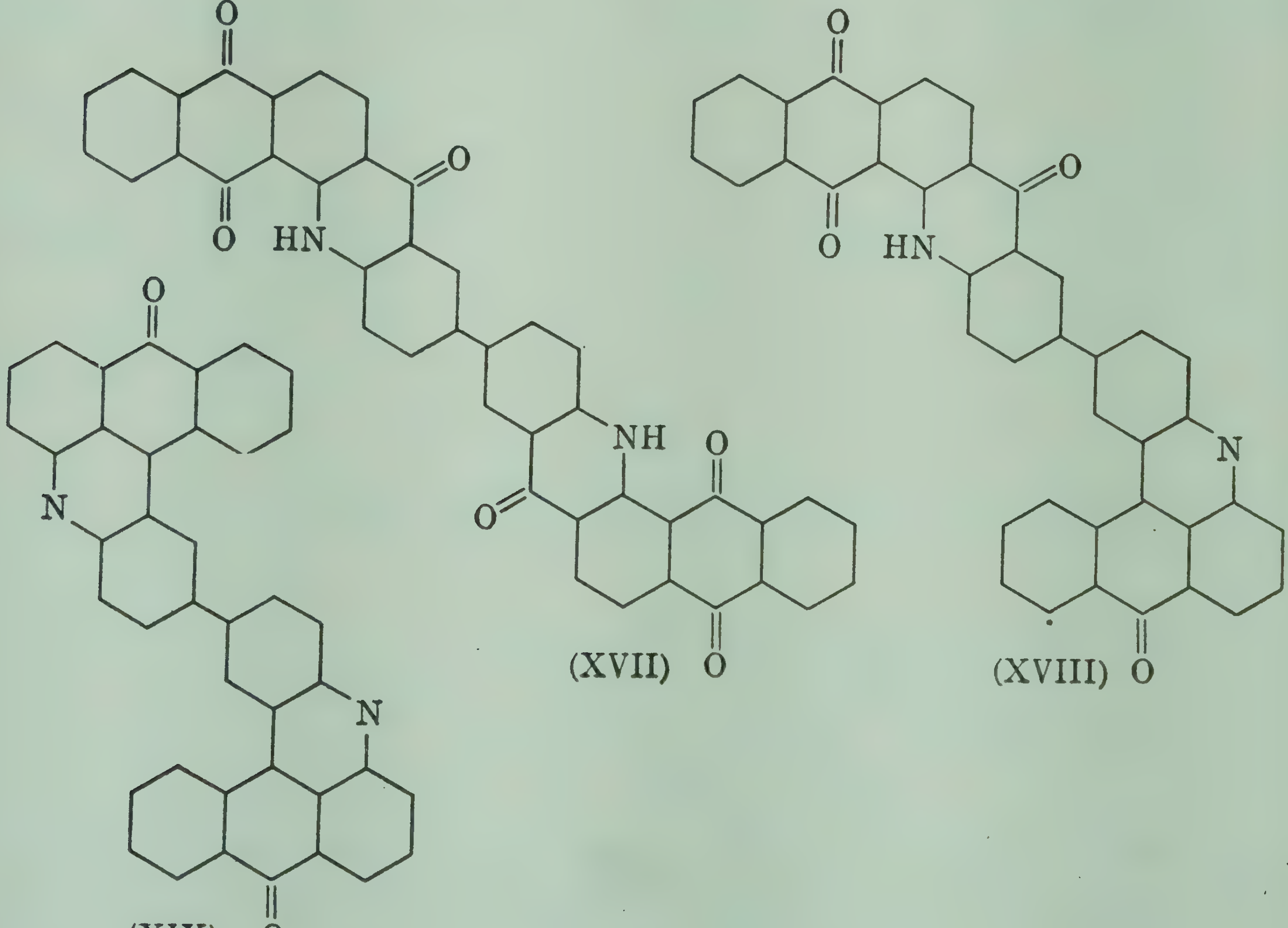

CO
Cl
COOH
COOH
96% H_2SO_4, 20% oleum, 105°, 6 hrs.
O
Cl
COOH
O
20% aq. NH_3,
Cu powder,
30– 40 atms.,
140°, 1 hr.
O
NH_2
COOH
O
1. PhCOOH, 20% oleum, 30–35°, 12 hrs.
2. 30% aq. NH_3, 7–20°, 18 hrs.
3. 30% aq. NaOH, 100°, 4 hrs.
4. 78% H_2SO_4, $NaNO_2$
O
N
Ph
N
OH
O
PCl_5, $PhNO_2$, 100–110°, 2 hrs.
O
N
Ph
N
Cl
O
Cl
O
HN
O
NH_2
O
PhCOCl, *p*-toluenesulfonic acid, naphthalene, 210°, 5–6 hrs.
O
O
O
O
N
Ph
N
NH
NH
O
Cl

Indanthrene Green 4G

yellow dye. A dye of great interest for this reason and for its constitution as a quinazoline derivative[168] is Indanthrene Green 4G (Chart 6).[3] It dyes green from a brown hydrosulfite vat; the fastness grades are: light 7, chlorine 4–5, and soda boil 4. By condensing the blue 6-amino derivative of (I) with 2-*p*-bromobenzamidoanthraquinone, the product (XVI) is a bright, clear green dye.[169] Condensation of the 6-amino derivative of (I) with 2-(4-bromo-1-naphthyl)anthraquinone-2,3′-oxazole gives a yellowish olive-green dye.[169a] Yellowish green dyes are obtained



(XVI)



(XVII)

(XVIII)

(XIX)

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[168] Cf. IG, BP 476,599; 494,168; USP 2,187,812.

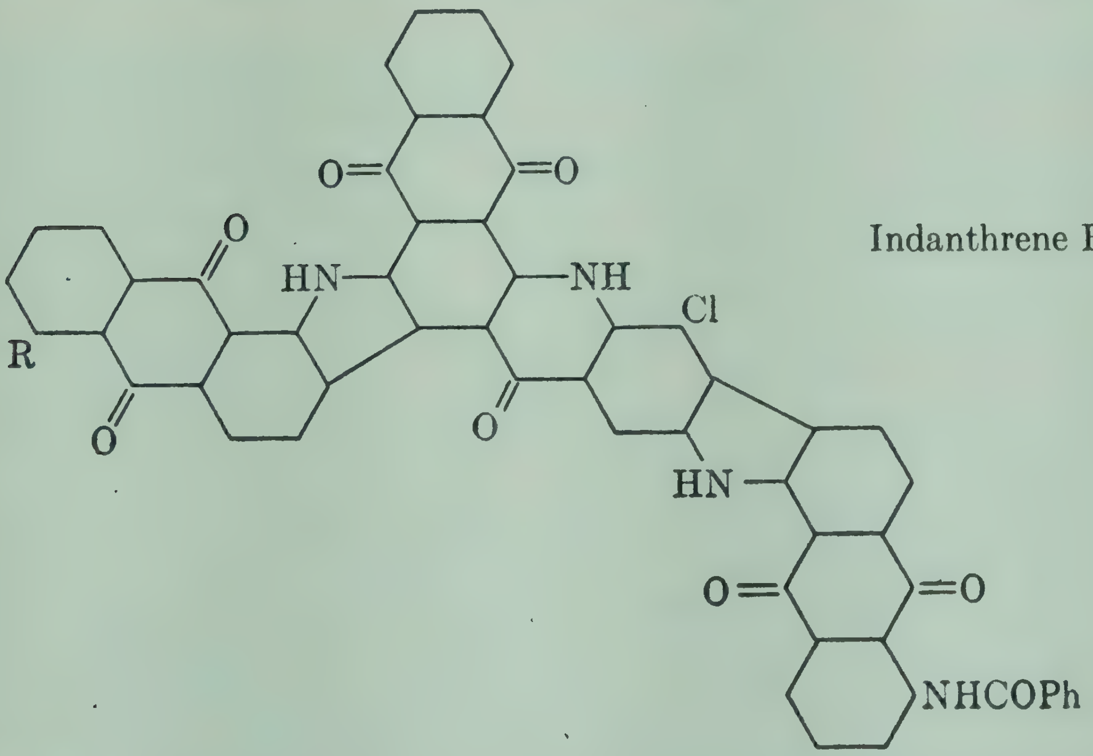
[169] Fairweather and ICI, BP 584,819.

[169a] Irving and ICI, BP 611,786. See also IG, FP, 835,268.

by condensing 1-chloroanthraquinone-2-carboxylic acid with 8-amino-3-alkoxypyrene, and cyclization of the intermediate product.[170]

Indanthrene Red Brown R is a complex dye prepared by an application of a general method for the synthesis of the anthraquinone-acridones, but the reaction proceeds in the expected manner only to the extent of about 20%. When 1-nitroanthraquinone-2-carboxylic acid is heated with benzidine, magnesium oxide, and water, and the product is heated with sulfuric acid for cyclization, it is found that a carboxylic acid is still present. On decarboxylation by heating with 2% caustic soda solution under pressure at about 160° for a few hours, a dye is ultimately obtained, which dyes a fast red-brown shade (light 6; soda boil 3–4) from a red-brown vat, and is considered to be a mixture of the expected diphthaloyldiacridonyl (XVII) (23%), the acridonylceramidone (XVIII) (70%) and the diceramidonyl (XIX) (7%).[3]

Indanthrene Brown 3GT is an anthraquinone-acridone-carbazole,[171] prepared by condensing Indanthrene Red Violet RRK or trichlorinated (I) with one mole of 1-amino-5-benzamidoanthraquinone, and cyclizing to a carbazole.[3] The dye has the maximum all-round fastness among the acridones (light 7–8; chlorine 5; soda boil 4–5). Indanthrene Brown NGR and IVGR are two closely related dyes,[2, 4] which contain an acridone and two carbazole ring systems. In the appended formula for Brown NGR (R=H), Brown IVGR is the derivative in which R is PhCONH. The dyes are prepared by condensing the 6-bromo-10,12-dichloro derivative of (I) with one mole of α-aminoanthraquinone and one of 1-amino-5-benzamidoanthraquinone, or two moles of the latter, and carbazolizing.



Indanthrene Brown NGR

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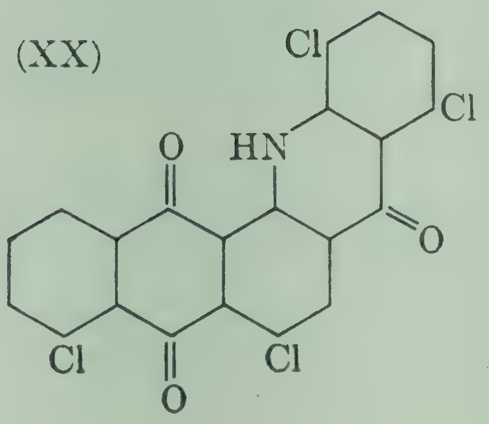
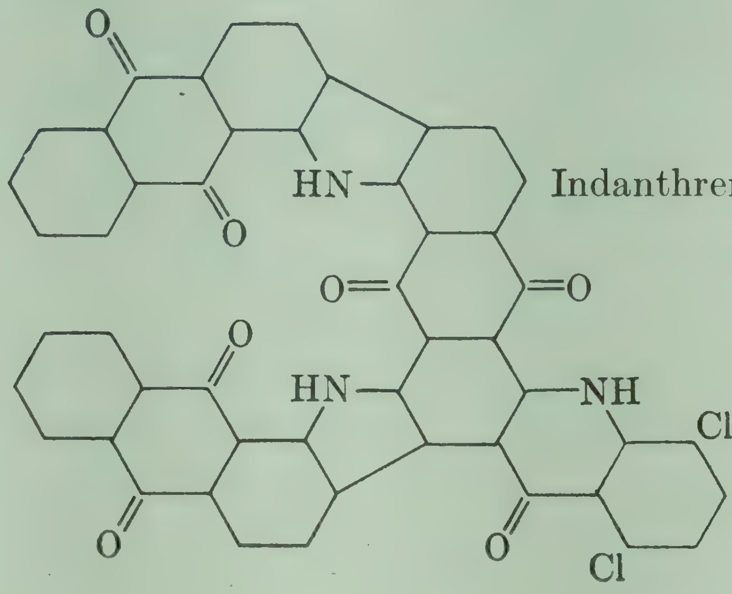
[170] Ciba, SP 216,314–7.

[171] Cf. IG, DRP 465,835; 509,423–4; 513,045; 513,475.

A recent and important IG development is the khaki dye, Indanthrene Khaki GR, which is claimed to be superior to Indanthrene Khaki GG in solubility, levelling power and fastness to mercerization, washing, alkali boil, and perspiration.[4, 148] Like Brown NGR and IVGR, it is a mixed carbazole-acridone, and is prepared by chlorination of the dichloroacridone obtained by the condensation of 1-nitroanthraquinone-2-carboxylic acid and 2,5-dichloroaniline by means of sulfur chloride and sulfuryl chloride in presence of iodine, when the tetrachloro compound (XX) is formed; condensation of (XX) with 2 moles of α-aminoanthraquinone and carbazolization give Khaki GR.

(XX)





Indanthrene Khaki GR

The patent literature contains many examples of mixed carbazole-acridones.[171a] Thus an acridone containing an anthrimide group (e.g., the condensation product of the 6-amino derivative of (I) and 1-chloro-4-benzamidoanthraquinone) may be cyclized to a carbazole.[172] Brown and gray dyes of very good fastness to light and bleach are obtained by condensing (I) containing a *p*-bromobenzamido group in the 6-position with an anthraquinone-carbazole containing an amino group,[173] and by similar methods leading to anthraquinone dyes of the structure XNHYNHZ in which X is (I) attached to the adjacent NH group in the 1,2,3,4,6 or 7-positions, Y is COAr or ArCO (Ar being an arylene radical) and Z is an anthraquinone-carbazole derived from 1-arylaminoanthraquinone attached to the adjacent NH in the 4,5 or 8-position. Carbazoles from trianthrimides having an acridone group present in one nucleus, e.g., 1(*N*),2-benzacridonyl-5,5′,1′,1″-, -5,8′,1′,1″-, -8,5′,1′,1″-, and -8,8′,1′,1″-trianthrimides, are brown dyes with high fastness properties. The trianthrimides are prepared by condensing one mole each of 1-aminoanthraquinone and the 4-amino derivative of (I) with 1,5-dichloroanthraquinone, and by similar methods.[174]

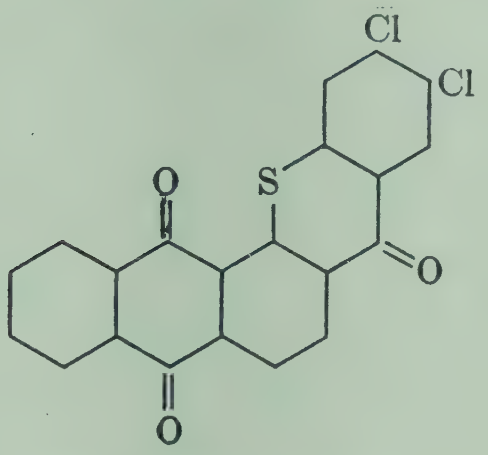
[171a] See also Max and Randall, BP 627,519; USP 2,467,561.

[172] du Pont, USP 2,036,663; Dettwyler and du Pont, USP 2,373,817.

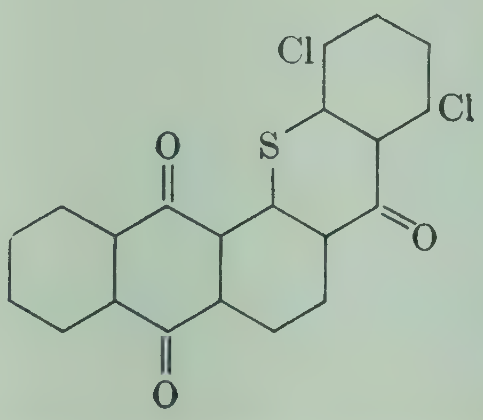
[173] Lodge and ICI, BP 566,872. See also ICI, USP 2,414,155.

THIOXANTHONES

The thioxanthones are a very small class, similar to the acridones in constitution and methods of preparation, but they are lighter in color and have feebler tinctorial power. Two examples among commercial dyes, both of which are now obsolete, are Indanthrene Golden Orange GN (CI 1164) and Indanthrene Yellow GN extra (CI 1165). They are prepared by the condensation of 1-chloroanthraquinone-2-carboxylic acid with 3,4- and 2,5-dichlorothiophenol respectively, and cyclization by means of sulfuric acid.[175] Orange to red vat dyes of good fastness to chlorine and light, which have printing properties, are obtained by condensing the 6-amino derivative of Indanthrene Golden Orange GN with 1-chloro-4- or -8-benzamidoanthraquinone and cyclizing to the carbazole by aluminum chloride in pyridine or nitrobenzene.[176] Orange to brown vat dyes containing the anthraquinone, thioxanthone and carbazole ring systems have been recently described.[177]



Indanthrene Golden Orange GN



Indanthrene Yellow GN extra

ANTHRAQUINONEAZINES (INDANTHRONES)

Indanthrone (Bohn, 1901; CI 1106), the first anthraquinone vat dye, continues to be manufactured on a large scale. Some of the current commercial names are Blue R, RS, RSN or RNS with the prefix of the name (Indanthrene, Caledon, etc.) of the various manufacturers for this class of dye. Indanthrone shades on cotton have excellent fastness to light and to boiling alkali, but the fastness to chlorine is poor, the beautiful reddish blue changing to an unattractive greenish blue. In spite of this defect, indanthrone is extensively used because of the beauty of the shades for which no exact equivalent is available.

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[174] Miller and Allied Chemical and Dyestuff, USP 2,315,537.

[175] BASF, DRP 243,750; 258,561. See also IG, DRP 475,688; 516,398.

[176] Dettwyler and du Pont, BP 561,754. See also du Pont, USP 2,344,981.

[177] Max, Randall, and General Aniline and Film, USP 2,428,758–9; 2,495,014.

Indanthrone is prepared by the alkali fusion of β-aminoanthraquinone; this is a complex reaction in which indanthrone is accompanied by a number of by-products, but the constitution of indanthrone has been conclusively established by analytical evidence and by several unambiguous syntheses.[178] From the elementary analysis and the molecular weight by the boiling point method in quinoline, the molecular formula was found to be $C_{28}H_{14}O_4N_2$, indicating that the dye was produced from two moles of β-aminoanthraquinone by the loss of four atoms of hydrogen ($2C_{14}H_9O_2N \rightarrow C_{28}H_{14}O_4N_2 + 4H$). The absence of a primary amino group and of an azo group, as judged by the usual reactions, and in particular the remarkable stability of the compound, indicated that the nitrogen atoms were present in a ring system, probably as a 1,4-diazine. The real proof came from synthesis. Thus, Bohn (1903) obtained indanthrone by heating 1-amino-2-bromoanthraquinone in nitrobenzene solution under the conditions of the Ullmann reaction. Scholl[178] suggested that the formation of dihydroindanthrone by fusion of β-aminoanthraquinone with caustic potash is probably preceded by the formation of the dihydro derivative of 2-amino-1,2′-dianthraquinonylamine. In support of Scholl's theory of the formation of indanthrone and flavanthrone, Lulek found that 2,2′-hydrazoanthraquinone underwent a rearrangement analogous to the semidine transformation, yielding 2-amino-1,2′-dianthraquinonylamine and 2,2′-diamino-1,1′-dianthraquinonyl; the former led to indanthrone and the latter to flavanthrone (see Chapter XXXII).[178]

The mechanism of indanthrone formation from β-aminoanthraquinone involves the dissociation of hydrogen from the amino group; two of the anions then condense to indanthrone. Resonance stabilization of the negative ion (IA) as a result of the contribution of the structure (IB) explains the repulsion of a proton from β-aminoanthraquinone as well as the intermolecular condensation of (IB) to indanthrone.[178a]

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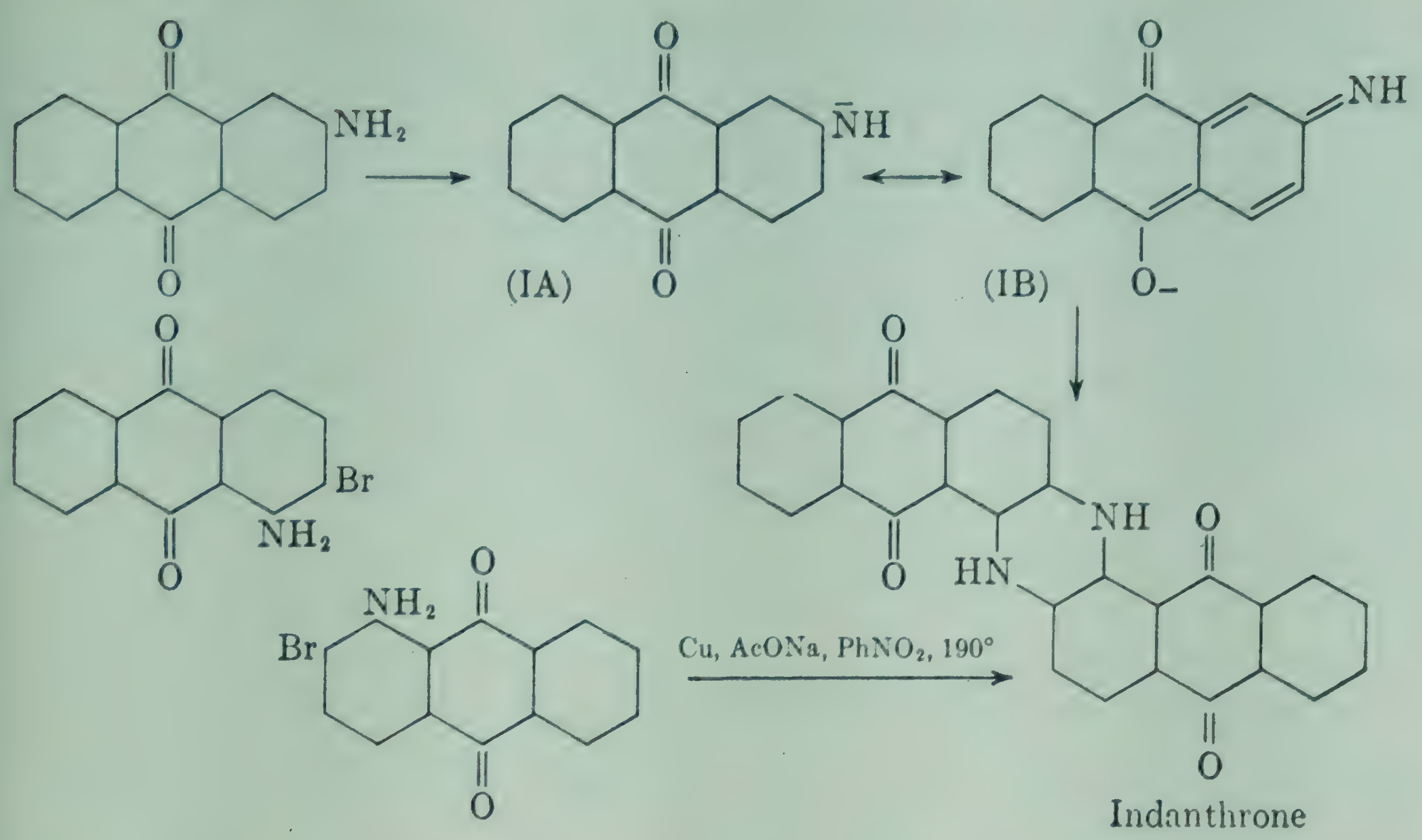
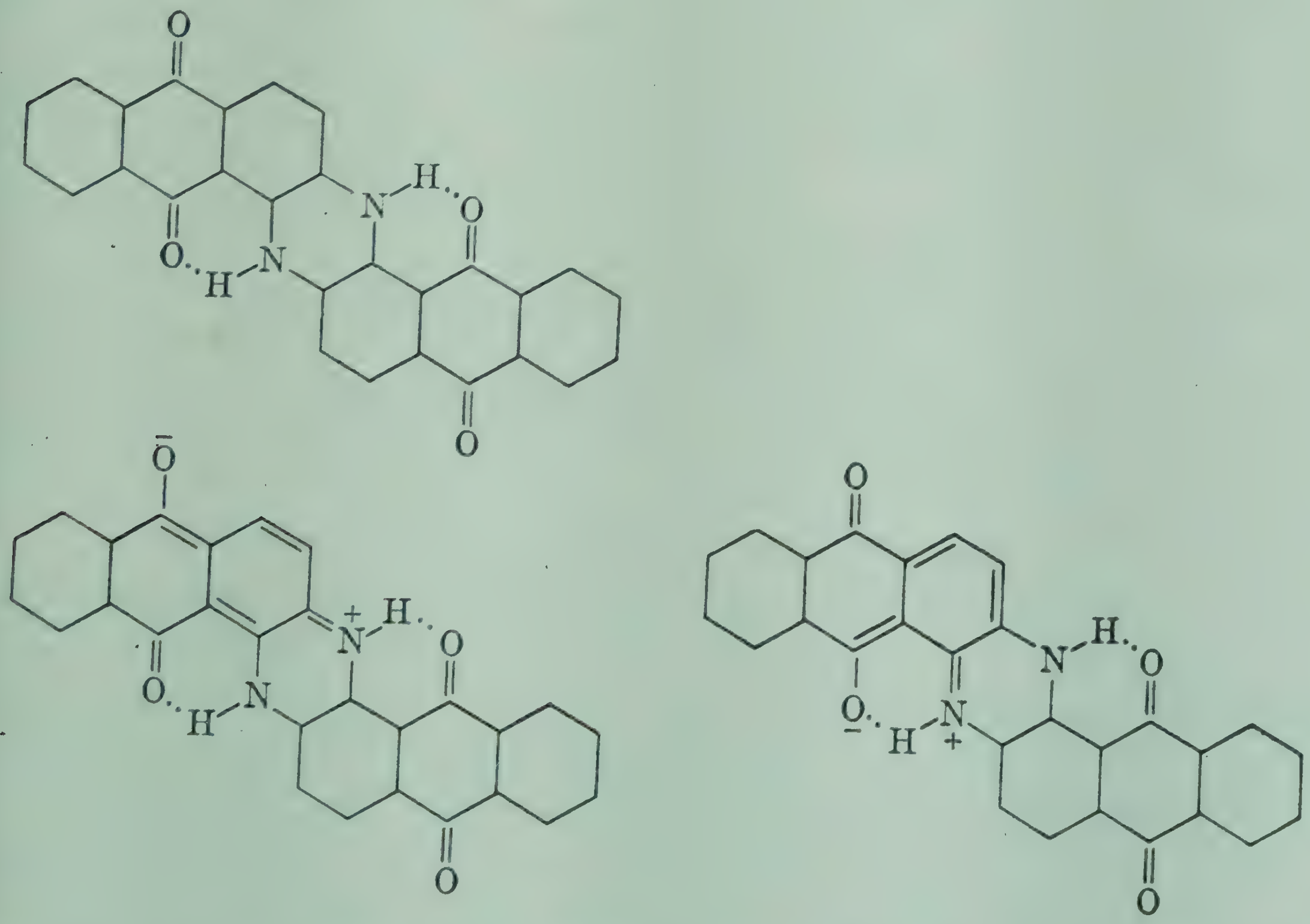
[178] Scholl *et al.*, *Monatsh.* **32,** 1035 (1911); *Ber.* **36,** 3410, 3427, 3710 (1903); **40,** 320, 326, 390, 395, 924, 933 (1907); Bohn, *ibid.* **36,** 1258 (1903); **43,** 999 (1910); Kaufler, *ibid.* **36,** 930, 1721 (1903); see also Lulek, *J. Soc. Dyers Colourists* **43,** 370 (1927).

[178a] Bradley (private communication) has recently carried out extensive experimental work on the mechanism of the formation of indanthrone and flavanthrone. He also postulates the ion (IA) as the first stage; addition of β-aminoanthraquinone in the 1-position leads to 2-amino-1,2′-anthrimide and ultimately to indanthrone. He suggests the isomerization of (IA) to β-aminoanthraquinone with the anionic charge in the 1-position, followed by the addition of β-aminoanthraquinone to form 2,2′-diamino-1,1′-dianthraquinonyl, as the intermediate stages in the formation of flavanthrone. See also Bradley *et al.*, *JCS* 2129 *et sequa* (**1951**).



The intimate relation of indanthrone to 1,2′-dianthrimide is shown by the fact that the latter can be converted by nitration, reduction and loss of ammonia to indanthrone. Fusion of β-aminoanthraquinone with alkali and an oxidizing agent under certain conditions yields 2-amino-1-hydroxyanthraquinone and 2-amino-1,2′-dianthrimide; the latter yields indanthrone on further treatment.[179]



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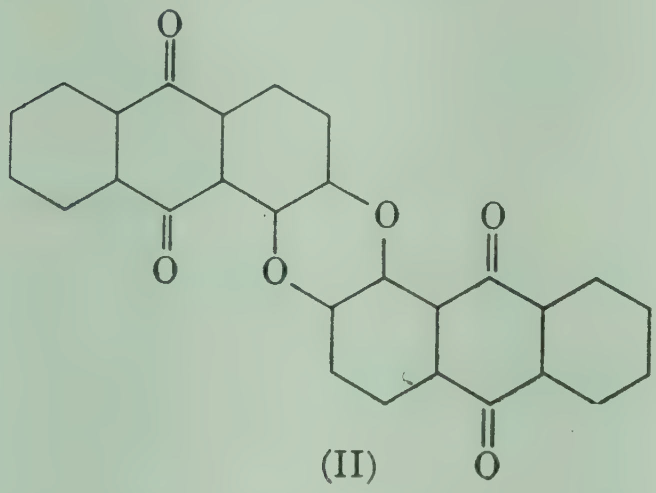
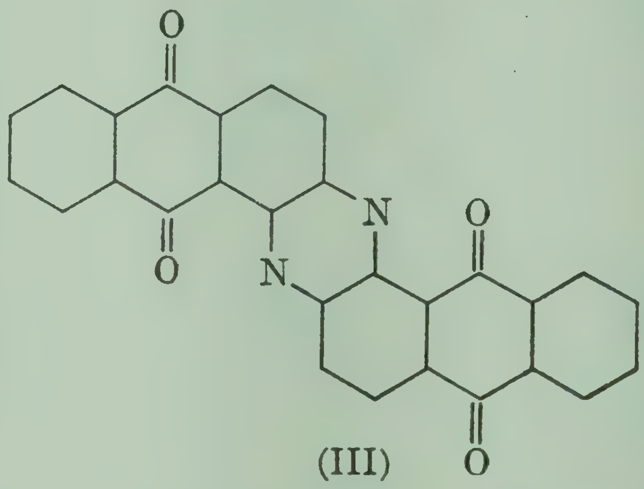
[179] Tanaka, *J. Chem. Soc. Japan* **56,** 192 (1935). See also Wittenberger, *Österr. Chem. Ztg.* **50,** 58 (1949).

Indanthrone is sparingly soluble in most solvents, but can be crystallized from quinoline or *o*-dichlorobenzene in characteristic curved needles which have a bright copper reflex. It is a compound of great stability, which is not decomposed by heating to 500°, or to 400° with concentrated hydrochloric acid, or by fusion with caustic potash at 300°. The intense blue color of indanthrone and its stability can be ascribed to resonance among the indicated structures and numerous others.

The dioxin analog (II) of indanthrone, which may be prepared by heating alizarin with 1,2-dichloroanthraquinone at 300° in presence of a mild alkali, is a yellow dye.[180]



(II)



(III)

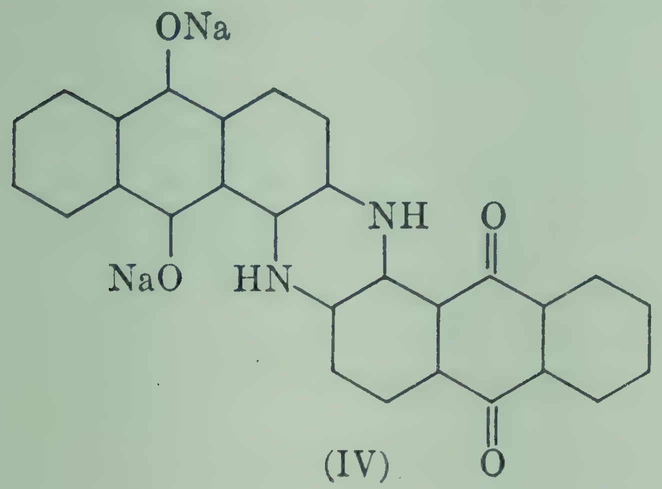
Reduction of indanthrone with phosphorus and hydrogen iodide, or by zinc dust distillation, yields anthrazine. Intermediate products of reduction have also been isolated by Scholl. By oxidation with chromic anhydride in boiling glacial acetic acid, one anthraquinone residue breaks down, and a 50% yield is obtained of 2,3-dihydroxy-7,8-phthaloylquinoxaline (see later), the constitution of which follows from its synthesis by the condensation of 1,2-diaminoanthraquinone with oxalic acid at about 170°.[181] Milder oxidation of indanthrone, for instance with hypochlorite solution, gives the yellowish green azine (III), which accounts for the low fastness of indanthrone shades to bleaching; but treatment of the dyed fiber with hydrosulfite regenerates the blue shade of the parent dye.

While indanthrone contains two anthraquinone residues, it only requires two hydrogen atoms (or two equivalents of a reducing agent such as hydrosulfite and alkali) to convert it into a leuco compound, unlike other polyanthraquinonoid vat dyes which usually take up in the process of vatting as many hydrogen atoms as there are carbonyl groups. Indanthrone is dyed by the hot or IN process, and under the correct conditions of vatting with hydrosulfite and caustic soda the disodium salt of the dihydro derivative, to which Scholl assigned the structure

[180] IG, BP 386,773.

[181] Scholl and Edlbacher, *Ber.* **44,** 1727 (1911).

(IV), is formed; the vat is blue in color and possesses good affinity for cotton. In preparing the indanthrone vat and applying it to the fiber, careful control of the concentration of dye, hydrosulfite and caustic soda, and of the temperature, is necessary. The disodium salt of the dihydro (or normal leuco) derivative of indanthrone is sparingly soluble and it may separate if the concentration of dye is too high. With a deficiency of caustic soda leucoindanthrone tends to tautomerize to a still less soluble form, probably the oxanthrone (V),[182] and it is therefore necessary to maintain an adequate concentration of caustic soda. Dyeing is carried out at about 60°; at higher temperatures duller shades and lower color values are obtained as a result of over-reduction. If there is excess of alkali present at the end of the dyeing process, when air oxidation of the leuco compound has been completed, duller and greener shades are produced by partial oxidation of the dye to the azine (III); the alkali must therefore be washed off immediately after dyeing and before air oxidation. An addition of hydrosulfite or glucose to the soaping bath is often made for brightening and reddening the shade.



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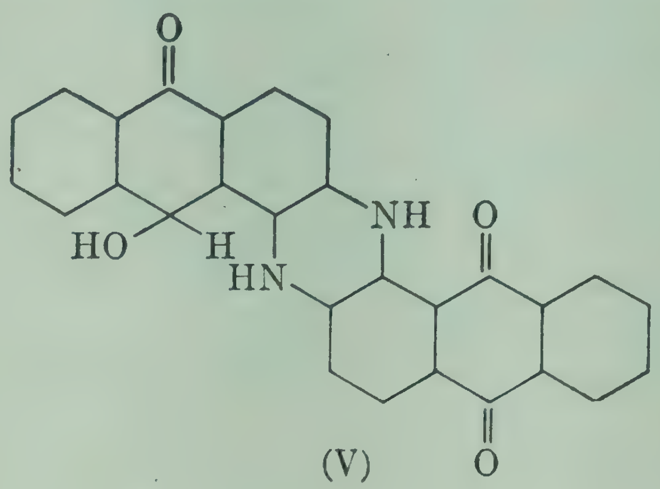

(V)

The reduction of indanthrone beyond the stage of the normal leuco derivative results in the blue vat changing ultimately to a yellow-brown. Scholl showed that, depending on the nature and quantity of the reducing agent, temperature and time, a variety of products can be formed, some of which he considered to be (VI), (VII) and (VIII). Müller, however, has found that at 90° four moles of hydrosulfite (or 8 atoms of hydrogen) are required to produce the end product, which he therefore formulated as (IX); this compound is insoluble and is not capable of reoxidation to indanthrone.[183] The yellowish brown solution of the tetrasodium salt of the tetrahydro derivative (VI) regenerates indanthrone only partially by oxidation with atmospheric oxygen, and it has poor substantivity for cellulose.

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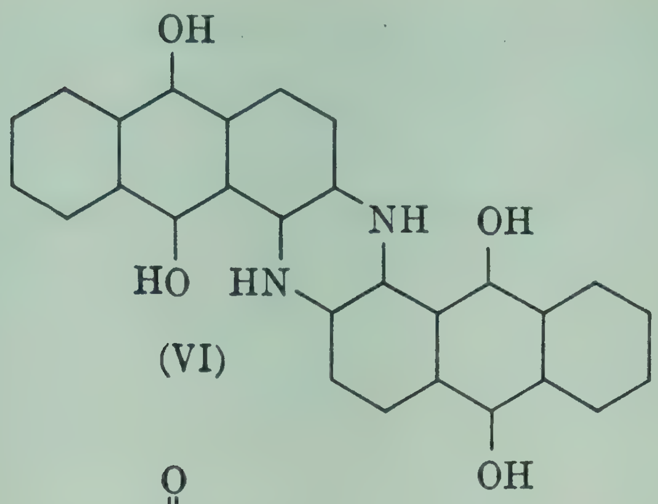
[182] See á Brassard, *J. Soc. Dyers Colourists* **59,** 127 (1943).

[183] *Melliand Textilber.* **28,** 93 (1947).



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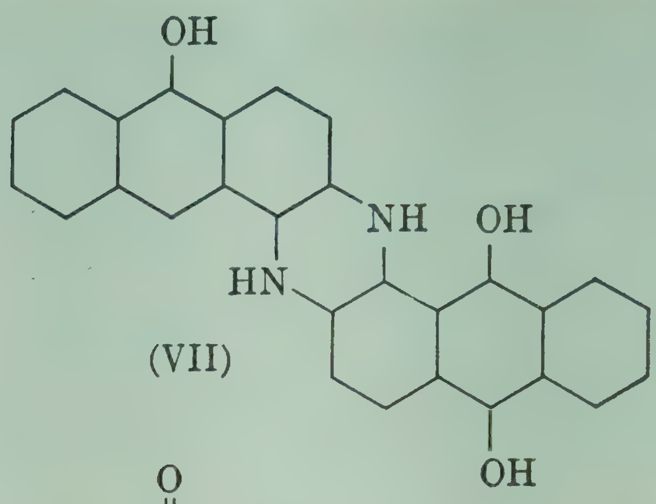

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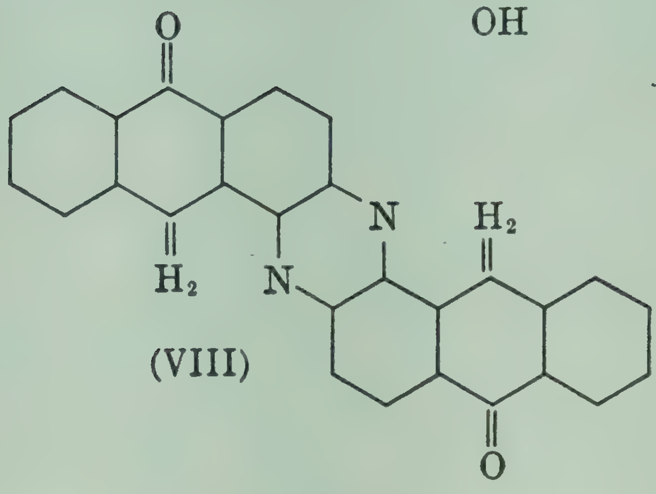

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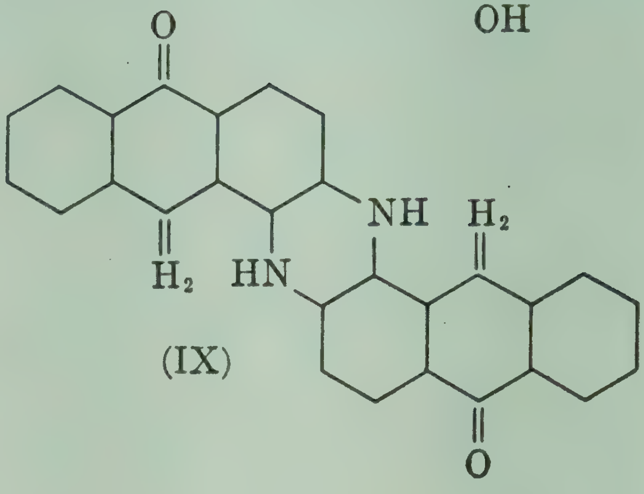
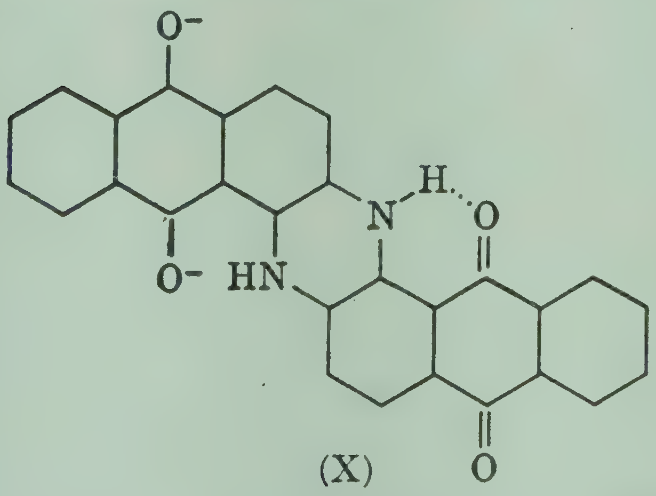
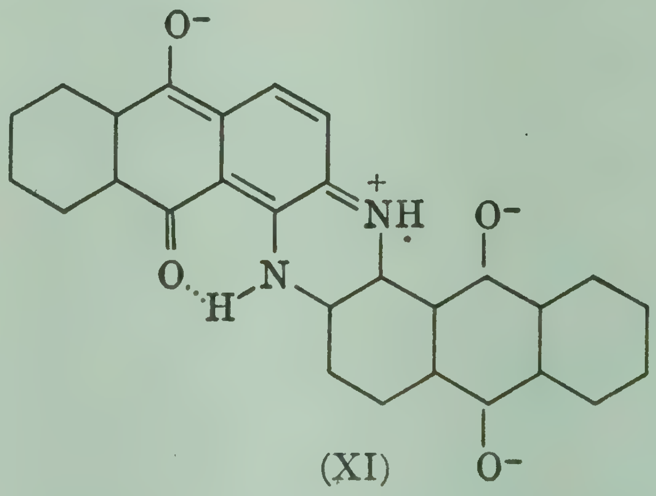


(IX)

The constitution of the blue dihydro derivative of indanthrone is of great interest. Although there is evidence of the formation of products of half reduction of other vat dyes containing more than one anthraquinone nucleus, and of the formation of semiquinones from anthraquinone itself and its derivatives,[184] indanthrone is distinguished from other diquinones by the much greater energy of reduction of the dihydro to the tetrahydro compound. The stability of the dihydro derivative of indanthrone results from the resonance of the ion among such structures as (X) and (XI), in addition to those which can be postulated for other dyes containing two anthraquinone ring systems.[184] The two



(X)



(XI)

imino groups of the dihydropyrazine ring are thus involved in the characteristic properties of indanthrone and its normal leuco derivative.

Technical method of preparation. While the blue alkali salt of leucoindanthrone is readily formed by fusing β-aminoanthraquinone with caustic potash at about 220°, very careful control of conditions is necessary for obtaining the maximum yield of indanthrone (indanthrene A), since the desired reaction is accompanied by side reactions leading to by-products. Alizarin is formed at too low a temperature of fusion, brown alkali-soluble products at a higher temperature, and yellow flavanthrone[185] at a still higher temperature. In addition, a second blue substance, indanthrene B, which has no dyeing properties, is always formed. Maki, who has made an extensive study of indanthrene fusion, considers indanthrene B to be a mixture of a blue-gray and a gray-green compound, the latter being called indanthrene C.[186] Indanthrene B is more soluble in organic solvents (e.g. nitrobenzene) than A or C. Tanaka[179] describes indanthrene B as a green compound possessing the structure of a dihydro-2′-amino-2-,1′-dianthraquinonylamine.[186a] Indanthrene B is readily separable from indanthrone since the disodium salt of the normal leuco derivative of the latter is much less soluble; further, the formation of indanthrene B is almost completely avoided by the addition of an oxidizing agent. Uniform conditions of temperature and concentration of reactants throughout the reaction mass are obviously favorable for obtaining reproducible results, and the addition of such substances as phenol, sodium acetate, glucose, and soybean protein[186b] as diluents has been suggested. Many of the patents on the production of indanthrone are therefore concerned with the addition of specific oxidizing agents and diluents and with the maintenance of conditions which reduce the formation of by-products to a minimum; but under the most favorable conditions the maximum yield is only about 50% of the theoretical amount.[187] Relatively pure indanthrone is usually isolated by taking advantage of the sparing solubility of the alkali salt of the leuco compound.

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[184] See Chapter XXX.

In the IG process[2] for Indanthrene Blue RS, a molten mixture of caustic potash (670 kg.), caustic soda (270 kg.) and water (3–4 kg.) is fed into a reaction kettle of nickel-iron (0.5% nickel). Anhydrous sodium acetate (220 kg.) is added, the kettle is evacuated and the air replaced by nitrogen (about 0.1 atm. pressure); the temperature is raised to 180°, and β-aminoanthraquinone (500 kg.; 86–87% purity) is fed in by means of a screw conveyor in the course of 20 minutes. A mixture of sodium nitrate (60 kg.), caustic potash (40 kg.) and caustic soda (20 kg.) is then added during 2–3 hours. At this stage the temperature of the melt is kept at 200–225°. The reaction mass is drawn into a vat containing water (11000 l.), and the reaction kettle rinsed out with more water (2000 l.). The mixture is cooled to 45–48°, and treated with 15% hydrosulfite solution (750 kg.). After two hours agitation, the potassium-sodium salt of leucoindanthrone, which crystallizes out, is filtered off in an enclosed continuous rotary filter in an atmosphere of nitrogen, and washed with a weak solution of hydrosulfite at 25–30° until the filtrate runs pale green. The filter cake is transferred into a rubber-lined vessel, stirred with water (1000 l.) and 50% caustic soda (20 kg.) and oxidized at 60° by air. The dyestuff is filtered, stirred at 60° with water (2000 l.) and 96% sulfuric acid (80 kg.), filtered in a filter press, washed neutral and dried. The yield is 56.5% of theory. The product may be directly marketed as Indanthrene Blue RS, or as Indanthrene Blue RSN after pasting with Tamol solution, drying on a double drum dryer, mixing with sodium carbonate and disodium phosphate, and powdering finely in a Raymond mill. A highly purified form of indanthrone, prepared by twice dissolving Blue RS in a mixture of 96% sulfuric acid and 20% oleum and drowning in water, is marketed as Indanthrene Brilliant Blue R (Caledon Brilliant Blue RN). Indanthrone in special physical form, suitable for the coloring of lacquer, paper and rubber, is prepared by partial reduction with glucose and reoxidation, and is marketed as Indanthrene Blue GGSP (for paper) and GGSLC (for lacquer).[2]

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[185] See Chapter XXXII.

[186] Maki, *J. Soc. Chem. Ind. Japan* **36**, Suppl. Binding No. 2, 44 (1933); and earlier papers; see also ref. 178.

[186a] Bradley, Leete and Stephens, *JCS* 2166 (**1951**), consider that indanthrene B is a mono- or dihydroxy derivative of the linear isomeride of indanthrone.

[186b] Shimada, *J. Soc. Chem. Ind. Japan* **45**, 6, 814, 817 (1942).

[187] Schwenk, *Chem. Ztg.* **52**, 45 (1928).

1-Chloro-2-aminoanthraquinones may be converted into indanthrones by condensation in presence of a catalyst (cuprous iodide) and an acid-binding agent.[188] The method used for preparing Soledon Blue 2RC is applicable to the synthesis of pure indanthrone; thus the disulfuric ester of 2-aminoanthrahydroquinone gives by alkali oxidation the tetrasulfuric ester of tetrahydroindanthrone, and subsequent oxidation under acid conditions gives indanthrone.[189] The sulfuric esters corresponding to both dihydro- and tetrahydroindanthrone have been prepared and characterized; the latter has been prepared by two methods; (1) treatment of indanthrone in sulfur trioxide and pyridine with iron filings,[189] and (2) alkaline oxidation of the disulfuric ester of 2-aminoanthrahydroquinone.[190]

Derivatives of indanthrone. Indanthrene Blue 3GF is prepared by condensing Blue RS with formaldehyde. Caledon Blue 3G and Brilliant Blue 3G are indanthrones containing hydroxyl and sulfonic groups, prepared by treating Brilliant Blue R with 100% sulfuric acid and boric acid at 90–95° for 8–10 hours.[18] Indanthrene Blue 3G (CI 1109; ST 1232) is similarly prepared, but the sulfonic group is split off by means of 92–94% sulfuric acid at 120°; it has also been stated that Blue 3G is prepared from crude Blue RS in the same manner as Brilliant Blue 3G from Brilliant Blue R. 4,4′-Dihydroxyindanthrone of definite constitution, Indanthrene Blue 5G (CI 1111), is prepared by the self-condensation of 2-bromo-1-amino-4-hydroxyanthraquinone (Thomaschewski, 1903); it is of little practical value as the greenish blue shade has very poor fastness to chlorine (1). This is also true of the bluish green dye (Indanthrene Green 2B; Caledon Green 2B; CI 1116) obtained by the self-condensation of 2,3-dichloro-1,4-diaminoanthraquinone; this intermediate is prepared by the action of sulfuryl chloride on leuco-1,4-diaminoanthraquinone in nitrobenzene solution at 35–45°. Green 2B has the further disadvantage of giving unlevel shades. Caledon Green RC, similarly prepared from 2-bromo-1-amino-4-anilinoanthraquinone,[18] has much better levelling properties, and slightly improved chlorine fastness (2).

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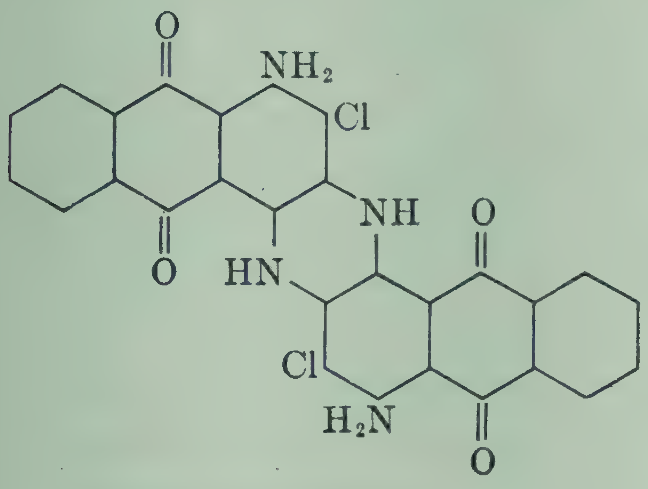
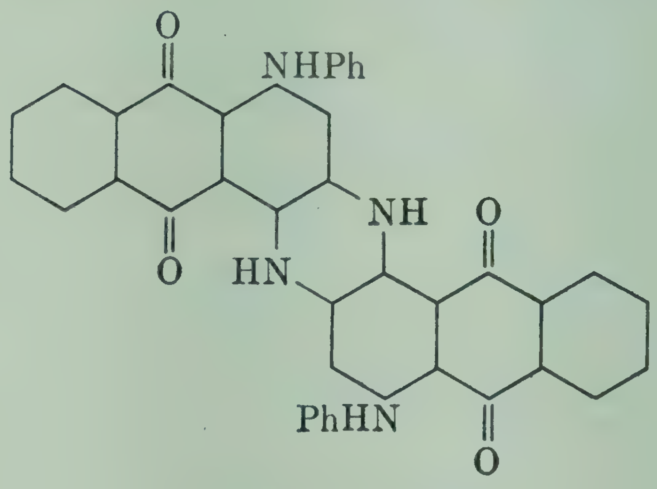
[188] Johnson and du Pont, BP 470,007.

[189] See Chapter XXXIV.

[190] Lyashenko and Kirzner, *J. Gen. Chem. U.S.S.R.* **16**, 583 (1946).



Caledon Green 2B



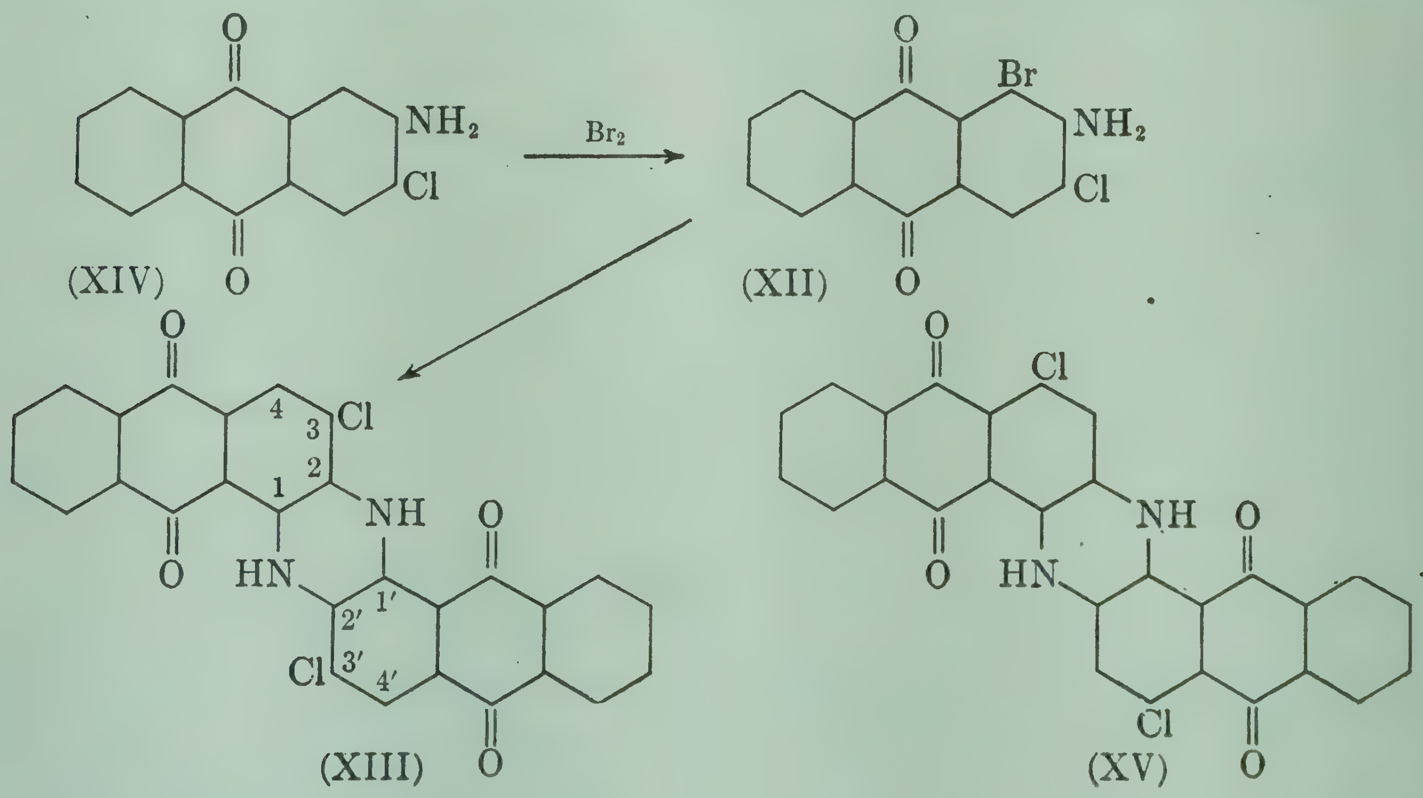
Caledon Green RC

Halogenated indanthrones. Soon after the discovery of indanthrone, Bohn (1902–1903) prepared its halogenated derivatives, the dibromo compound being marketed as Indanthrene Blue GC (BASF) or RC (IG) (Caledon Blue GC) and the chloro compound as Indanthrene Blue GCD (cf. CI 1112–5). The essential object of halogenation is to improve the fastness to chlorine without a material alteration in the indanthrone shade, and numerous patents have been taken on methods by which chlorinated indanthrones may be prepared. The chlorinated indanthrones are so important at the present time that in the U.S.A. their sale is many times that of the parent dye. A series of chlorinated indanthrones are now commercially available, e.g. Indanthrene Blue GCD, BC, RCL; Caledon Blue GCD, RC, BCD, GCP; and Alizanthrene Blue RC. There are two distinct routes to the chloroindanthrones.

The first is the chlorination of indanthrone, for which a wide variety of chlorinating agents and conditions (e.g., gaseous chlorine, sulfuryl chloride, antimony pentachloride, using nitrobenzene, sulfuric acid, oleum or chlorosulfonic acid as solvent) can be used; and the second is synthesis from chlorinated intermediates, specifically from 3-chloro-1-bromo-2-aminoanthraquinone (XII). Indanthrene Blue GCD is prepared by passing chlorine into a solution of indanthrone in 91.5% sulfuric acid in presence of a little manganese dioxide at 50–55° until the chlorine content of the product is 5 to 8%. Indanthrene Blue BC and BCS are prepared similarly, the chlorination being continued until the chlorine content is 13.8 to 14% (calc. for dichloroindanthrone: Cl, 13.9%); the difference between the two brands is in the method of purification by fractionation from sulfuric acid.

Direct halogenation of indanthrone attacks both the 3,3′- and 4,4′-positions, but chiefly the latter.[18, 113] A method of direct chlorination claimed to yield the 3,3′-derivative (XIII), and possessing the advantage that no higher chlorinated products are formed, is to heat indanthrone with sulfur dichloride. The dichloro compound thus prepared is also stated to have maximum bleach fastness. It has also been stated that (XIII) of high purity can be prepared by chlorinating indanthrone or 3,3′-dibromoindanthrone at 210–220° in trichlorobenzene in presence of sulfur;[191] and that a chlorinated product with the fastness properties of (XIII) is obtained by chlorination in nitrobenzene with iron and iodine as catalysts.[192]

Pure 3,3′-dichloroindanthrone (XIII) is obtained by the bromination of 3-chloro-2-aminoanthraquinone (XIV) to the 1-bromo compound



(XIV) (XII) (XIII) (XV)

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[191] du Pont, USP 2,413,483; 2,413,514.

[192] Knowles and Lycan, USP 2,205,418.

(XII), which is then self-condensed; and (XIV) may be prepared in one of two ways. The chlorobenzoylbenzoic acid obtained by the condensation of phthalic anhydride and chlorobenzene is nitrated, reduced and cyclized; the product is a mixture of (XIV) and 2-chloro-1-aminoanthraquinone, from which (XIV) can be separated by fractional precipitation from sulfuric acid solution. Caledon Blue RC is 3,3′-dichloroindanthrone prepared by this route.[113, 116] The second method is partial amination of 2,3-dichloroanthraquinone, used by IG for the preparation of Indigosol Blue IBC.[189] 3,3′-Dichloroindanthrone may be prepared from 1,3-dichloro-2-aminoanthraquinone by heating it in an inert solvent in presence of an acid-binding agent and a special cuprous halide.[193] Another route to (XIII) is the oxidation in substance of the tetrasulfuric ester of the tetrahydro derivative, Soledon Blue 2RC.[189]

Halogenated indanthrones are formed, instead of flavanthrone, if β-aminoanthraquinone is heated with antimony pentachloride in nitrobenzene in presence of selenium and a copper salt.[194] 6,6′,7,7′-Tetrachloro- and 3,3′,6,6′,7,7′-hexachloroindanthrones have been synthesized.[195]

There is some confusion in the literature regarding the constitution of the commercial dyes and the position of the chlorine atoms when the chlorination is effected by various methods.[196] Preparation from a halogenated intermediate, in which the orientation of the halogen atoms is definite, will give a chloroindanthrone of authentic constitution; but the position of the chlorine atoms in a product obtained by the direct chlorination of indanthrone needs to be proved. This is difficult because of the similarity of (XIII) and (XV) and the fact that an unambiguous synthesis of (XV) has not yet been achieved; but an indication of the probable orientation can be obtained from the properties. Halogenated indanthrones require much more careful control of dyeing conditions than the parent dye itself for obtaining level shades, partly because there is a possibility that by the action of hydrosulfite and alkali the halogen atoms may be removed by reduction or replacement by hydroxyl and mercapto groups. Thus a temperature not exceeding 50° is recommended for dyeing Indanthrene Blue BC. In the products of the direct chlorination of indanthrone, whether the chlorination is effected by means of gaseous chlorine or sulfuryl chloride or antimony pentachloride, the chlorine is more labile than in synthetic 3,3′-dichloroindanthrone, indicating that direct chlorination leads mainly to substitution in α-positions (4,4′ or 5,5′ or 8,8′). The 3,3′-dichloro compound approaches the shade of indanthrone closer than the products of direct chlorination, which are somewhat greener in tone. Caledon Blue GCD dyes a slightly greener shade than Caledon Blue RC, but the two are very similar in other properties, and it would appear that Caledon Blue GCD consists of synthetic 3,3′-dichloroindanthrone shaded with a green dye (Caledon Jade Green). Both types of chloroindanthrones have better fastness to chlorine than indanthrone (3–4 against 2), but there is little difference between the two types themselves in this regard. If, however, more vigorous oxidation is employed, such as successive treatment of the dyes on cotton with acid potassium permanganate solution and acid hydrogen peroxide,[197] significant differences are disclosed. Indanthrene Blue GCD and BC, as well as a dichloroindanthrone prepared by means of sulfuryl chloride, undergo a profound change to a greenish yellow, while synthetic 3,3′-dichloroindanthrone and a dichloroindanthrone obtained by means of antimony pentachloride are but slightly affected, changing to a more greenish blue. The greater resistance of 3,3′-dichloroindanthrone to oxidation to the yellow azine is obviously due to the neighborhood of the chlorine atoms and the imino groups. It is suggested that antimony pentachloride, which is specific in dichlorinating indanthrone even when an excess of the reagent is used, gives 4,4′-dichloroindanthrone (XV); and other methods of direct chlorination give 5,5′- or 8,8′-dichloroindanthrones. Substitution in the 4,4′-positions may be expected to retard oxidation to the yellow azine to a greater extent than substitution in the 5,5′- and 8,8′-positions which are more remote from the imino groups.[198]

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[193] Dettwyler and du Pont, USP 2,126,455–6.

[194] Burgoine, Soutar, and ICI, BP 414,136.

[195] Thomas, Thomson, Smith, and ICI, BP 358,078.

[196] See also Maki and Mine, *J. Soc. Chem. Ind. Japan* **47,** 522 (1944).

***N*-Alkylindanthrones.** The low fastness of indanthrone to chlorine is attributed to the sensitivity of the imino groups, resulting in the conversion of the dihydroazine to the azine, and in the expectation of obviating this defect, the *N*,*N*′-dimethyl and *N*-methyl derivatives (Algol Blue RK and Indanthrene Blue RK) were marketed (cf. CI 1108). They are prepared by the Ullmann reaction. Thus Indanthrene Blue RK is obtained by heating 2-bromo-1-aminoanthraquinone and 2-bromo-1-methylaminoanthraquinone with copper bronze, sodium acetate and magnesia in naphthalene solution at 200°. However, the *N*-alkyl compounds are not faster to chlorine than indanthrone itself, and it is probable that dealkylation takes place readily.

N-Alkylindanthrones form brown alkaline hydrosulfite vats, but when they are halogenated, faster products which dye in blue to blue-green shades from a blue vat are obtained.[199] 1,3-Dihalogeno-2-monomethylaminoanthraquinones, used for the preparation of halogenated

[197] See Ref. 32, Chapter XXX.

[198] Bedekar, Tilak, and Venkataraman, *Proc. Indian Acad. Sci.* **28A**, 236 (1948).

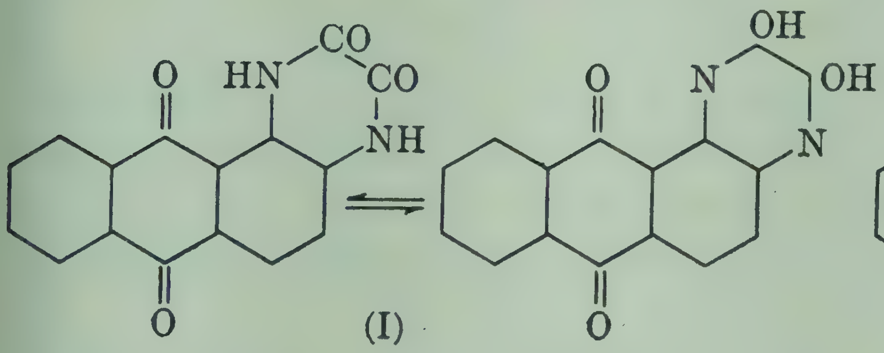
[199] IG, BP 440,822.

N,N'-dimethylindanthrones, are prepared by the prolonged action of formaldehyde and 97-98% sulfuric acid at moderate temperature on 1,3-dihalogeno-2-aminoanthraquinone.

The halogenation of *N*-alkylated *o*-amino-α,β-dianthrimides in organic solvents yields blue and bluish-green vat dyes which are probably halogenated *N*-alkylindanthrones.[200] *N*-Alkylindanthrones treated with dehydrogenating agents yield fast blue vat dyes of unknown constitution.[201] Fast blue dyes which are probably *N*-alkylindanthrones are obtained when *o*-amino-α,β-dianthrimides, in which the amino- and/or imino group has an alkyl substituent, are treated with oxidizing agents such as manganese dioxide and sulfuric acid or benzoyl chloride and iodine. The dyes are improved by halogenation.[202]

PHTHALOYLQUINOXALINES

Indanthrene Brilliant Scarlet RK is a phthaloylquinoxaline or a pyrazine fused to one anthraquinone nucleus instead of two as in indanthrone.[203] The intermediate (I), mentioned earlier as an oxidation product of indanthrone,[181] is prepared by heating 1,2-diaminoanthraquinone with oxalic acid at about 150°; when (I) is heated with *m*-toluidine and zinc chloride in nitrobenzene for a few hours, the dyestuff is formed.[2] Both the reactions proceed in nearly quantitative yield. Indanthrene Brilliant Scarlet RK has very high fastness to light (7) and to chlorine (5), but the fastness to alkali boil is of a somewhat lower degree (3–4). The indicated structure for Indanthrene Brilliant Scarlet RK is cited from a FIAT report, but the condensation of *m*-toluidine with the other hydroxyl group is not excluded.



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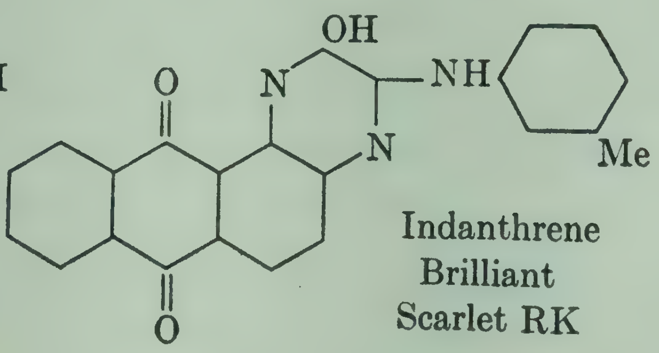

Indanthrene Brilliant Scarlet RK

The product (II) obtained by heating (I) with phosphorus pentachloride and then with 3,5-bis-trifluoromethylaniline is stated to be a new, nontendering, greenish yellow vat dye with light fastness 6–7.[24] In view of the considerable difference between the depths of color of (II) and Indanthrene Brilliant Scarlet RK, it is necessary to investigate the constitution of these dyes.

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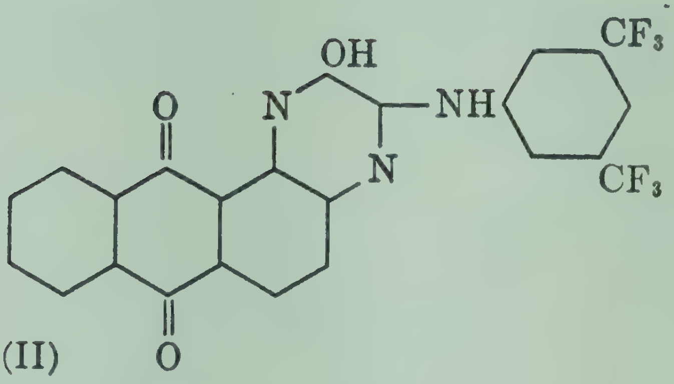
[200] IG, DRP Anm. J. 48,872.

[201] IG, FP 782,990.

[202] IG, DRP Anm. J. 48,878–9.

[203] IG, DRP Anm. J. 54,394; 55,167.

When the dichloro compound obtained by treating (I) with phosphorus pentachloride is condensed with suitable aromatic and heterocyclic amines blue, violet, red, red-brown, orange, or gray vat dyes are produced;[204] with *o*-diamino-, *o*-aminohydroxy- or *o*-aminomercapto-anthraquinones, the products are the vat dyes (III). Their fastness is improved by alkylation.[205]



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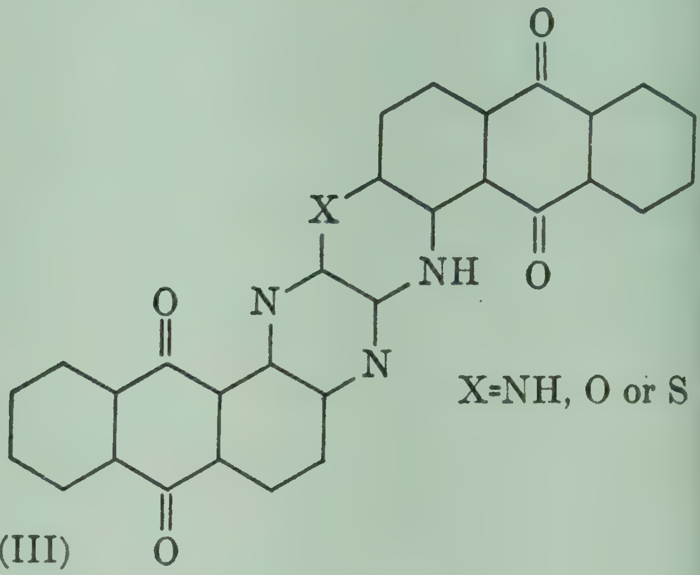
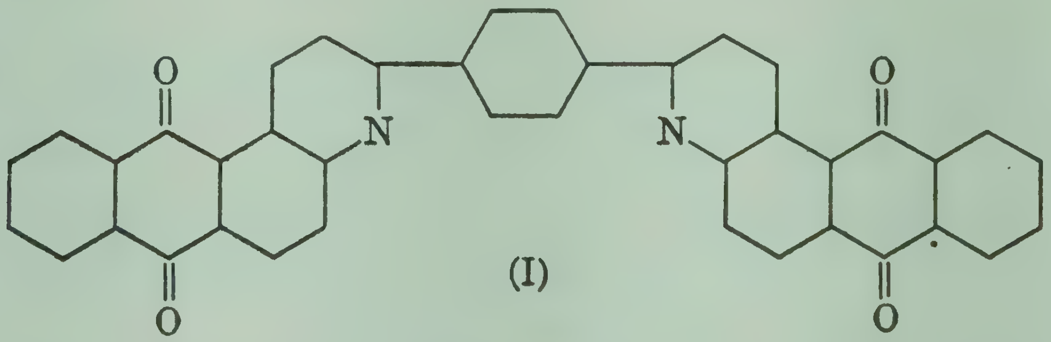


(III)

Miscellaneous Heterocyclic Compounds

In a new reaction for the preparation of pyridinoanthraquinones, Schiff's bases (including those from diamines and dialdehydes) are condensed with pyruvic acid; the products are decarboxylated and oxidized if necessary. The vat dye (I) from 2-aminoanthraquinone and terephthaldialdehyde is a fast greenish yellow.[206]



(I)

Violet, olive and gray dyes,[207] which may be diphthaloyl-benzodiazabenzanthrenes (II) or 8-α-anthraquinonylamino-3′,4′-phthaloylacridines (III), are obtained when α-anthraquinonylamides of 1-arylaminoanthra-

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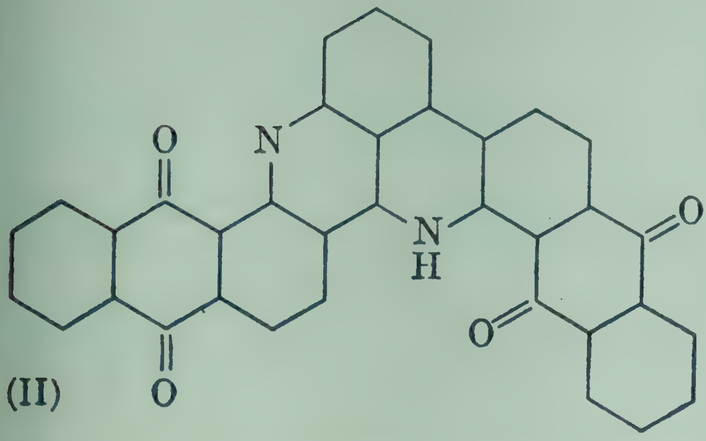
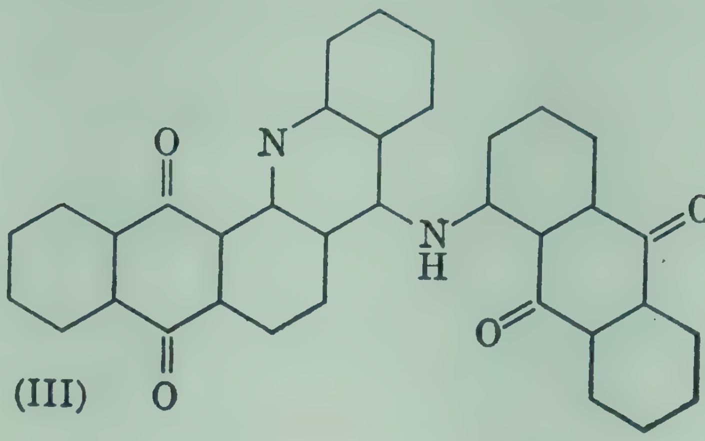
[204] IG, BP 454,882.

[205] IG, BP 464,299.

[206] IG, DRP Anm. J. 48,460. For examples of vat dyes containing pyrazole, pyrazine and pyrimidine ring systems, see IG, DRP 643,083; 645,010; 645,568; 650,750; 656,381; 672,493.

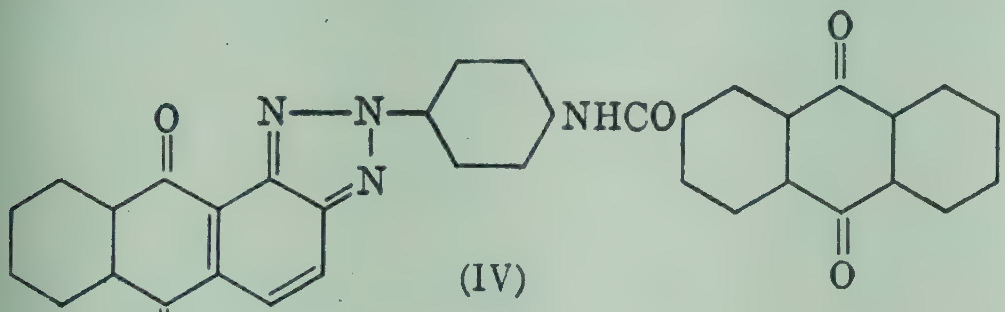
[207] DRP Anm. J. 51,699.

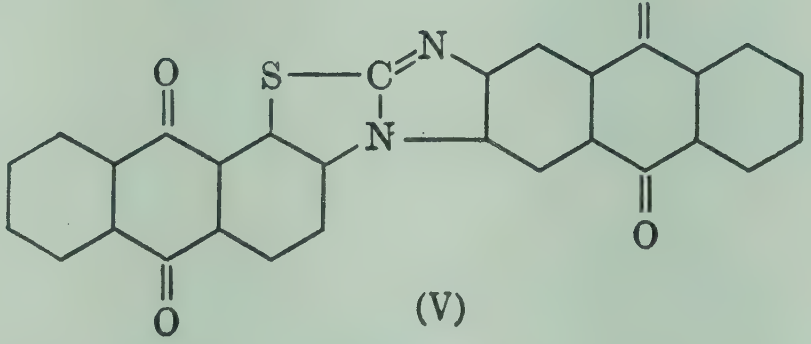

(II)


(III)

quinone-2-carboxylic acids, in which the *ortho* positions of the arylamino group are unsubstituted, are treated with sulfuric acid.

Vat dyes are obtained from 2-aminoanthracene by condensing with diazonium salts to obtain triazoles, which are oxidized to anthraquinones. When aromatic diamines are employed the products are yellow to brown vat dyes; and when diazotized *p*-nitroaniline is used, and the nitro group subsequently reduced and acylated with vattable acids or condensed with halogenoanthraquinones, yellow, orange, brown, or gray vat dyes, such as (IV), are obtained.[208]


(IV)


(V)

A reaction which appears to be general for anthraquinone derivatives having a homo- or heterocyclic ring in the 1,2-positions, or for anthrones with a homo- or heterocyclic ring in the 1,9-positions, is to condense them with vattable primary amines in presence of alkaline condensing agents. Anthraquinone-1,2-thiazoles condense with 3-bromo-2-aminoanthraquinone in two stages, yielding a product with probably both a thiazole and imidazole ring (V). Yellow, orange, red-brown, blue or gray dyes may be thus prepared, using suitable components.[209] The anthrone types which undergo this reaction include benzanthrone, anthrapyridones, anthanthrone, dibenzopyrenequinone and dibenzoperylenequinone, and the products include violet, corinth, brown, gray and olive vat dyes.[210]

[208] IG, BP 467,157; 468,686; 503,556.

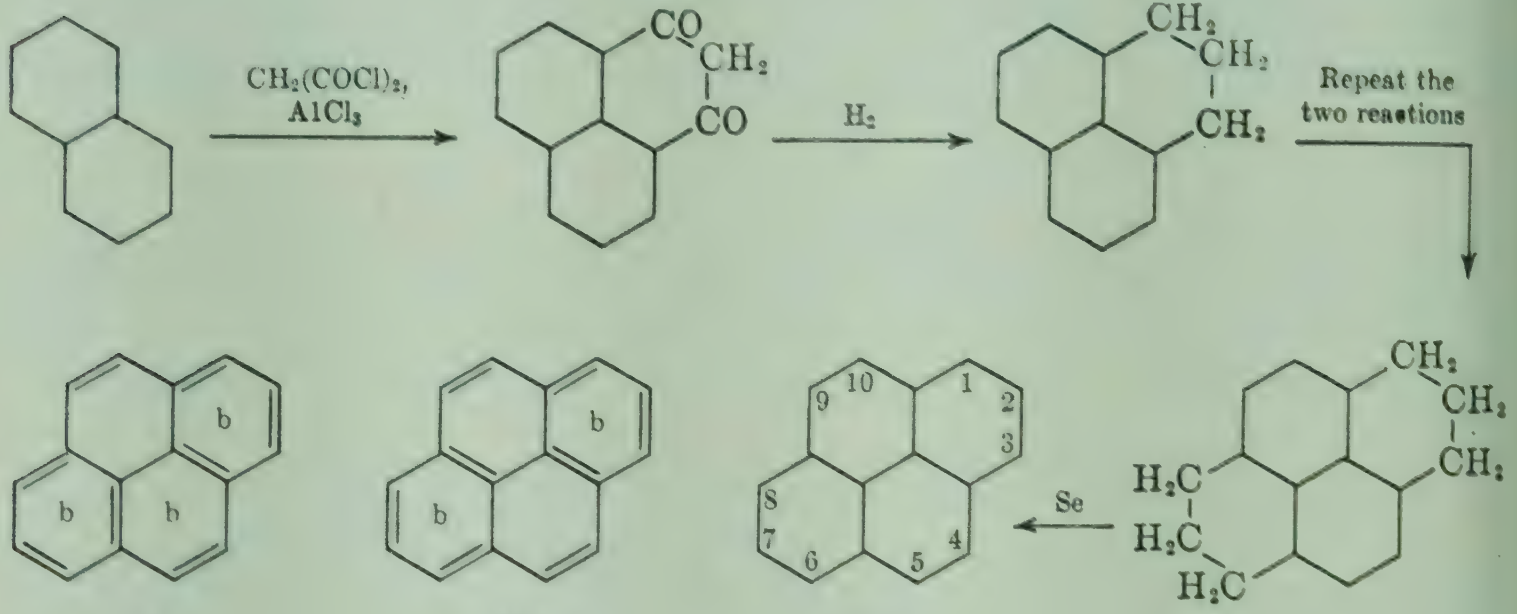
[209] IG, FP 803,279; see also FP 806,327.

[210] IG, BP 467,770.

Chapter XXXII

ANTHRAQUINONE VAT DYES—ANTHRONE DERIVATIVES

Many of the vat dyes[2–4a] grouped as anthrone derivatives contain the pyrene and perylene ring systems. The pyrene skeleton occurs in the dibenzopyrenequinones, the anthanthrones and the pyranthrones; and perylene in the violanthrones and isoviolanthrones.



(A) (B) Pyrene

Pyrene has been isolated from the coal-tar fraction boiling above 360°, and from "stupp fat" which is a by-product in the working up of certain bituminous mercury ores. Synthetically it can be made from naphthalene and malonyl chloride.[1] Refinements in the fractionation of coal-tar constituents have now made pyrene readily accessible as a possible raw material for vat dyes, such as pyranthrone, which contain the pyrene ring system, but are now prepared by other routes.

Pyrene crystallizes in colorless plates or leaflets, m.p. 148° (m.p. 156° corr.). Scholl and Vollmann[5] (Cb) and Kunz[6] (IG) have carried out

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[1] Fleischer and Retze, *Ber.* **55,** 3280 (1922). See also Braun and Rath, *Ber.* **61,** 956 (1928); Cook *et al.*, *JCS* 365 (**1934**); Chatterjee *et al.*, *J. Indian Chem. Soc.* **24,** 169 (1947).

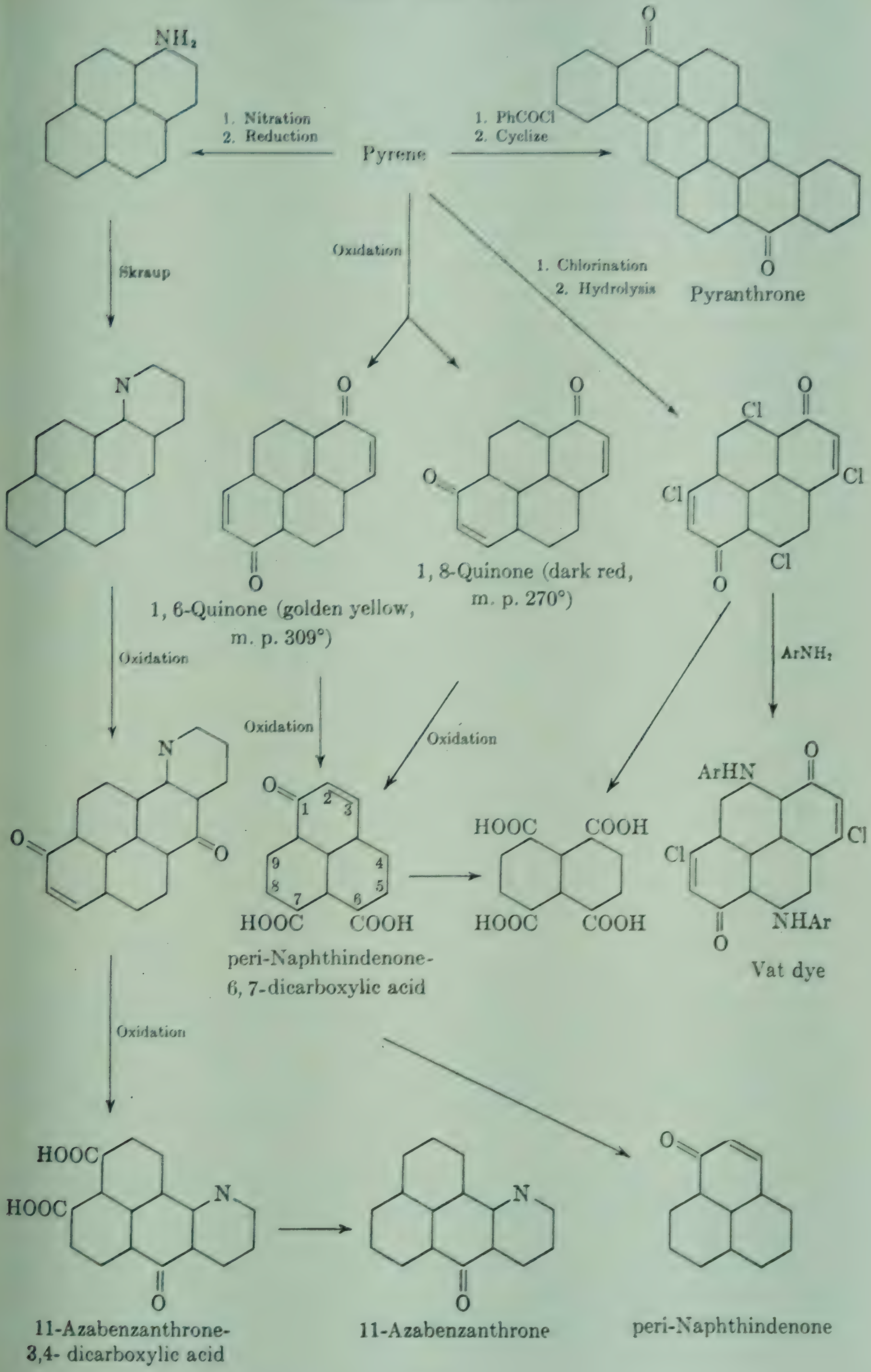
[2–4a] IG methods are described in *BIOS* (2) **987**; (3) **1493**; (4) Misc. Report **20**; and (4*a*) *FIAT* **1313** II.

[5] Vollmann, *et al.*, *Ann.* **531,** 1 (1937). See also IG, DRP 589,145; 648,111; DRP Anm. J. 49,775; BP 414,230; 434,128; 434,160; 441,408; 448,788; BP Appl. 3600/35; FP 796,765; Ciba, BP 431,105; 443,408; 447,096; SP 177,937.

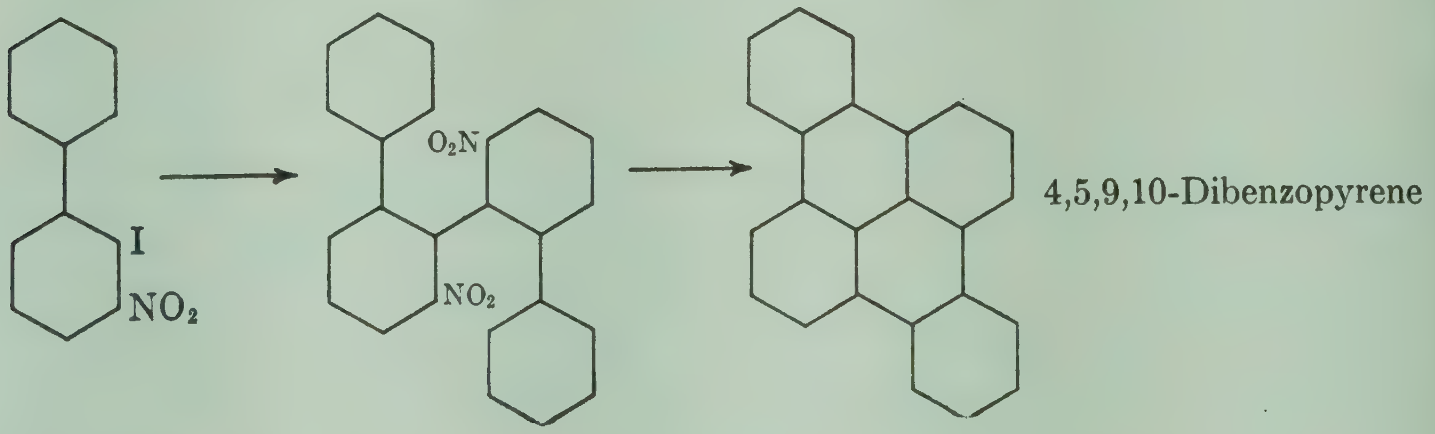
[6] Kunz, *Bull. Soc. Ind. Mulhouse* No. 3 (1934); *Angew. Chem.* **52,** 269 (1939).

CHART 1

SYNTHESES FROM PYRENE


NH$_2$
1. Nitration
2. Reduction
Pyrene
1. PhCOCl
2. Cyclize
Pyranthrone
Skraup
Oxidation
1. Chlorination
2. Hydrolysis
N
1, 6-Quinone (golden yellow, m. p. 309°)
1, 8-Quinone (dark red, m. p. 270°)
Cl
Oxidation
ArNH$_2$
Oxidation
Oxidation
1
2
3
4
5
6
7
8
9
HOOC
COOH
peri-Naphthindenone-6, 7-dicarboxylic acid
HOOC
COOH
HOOC
COOH
ArHN
NHAr
Vat dye
Oxidation
HOOC
HOOC
11-Azabenzanthrone-3,4- dicarboxylic acid
11-Azabenzanthrone
peri-Naphthindenone

extensive synthetical experiments and orientation studies on pyrene, some of which are illustrated in Chart 1. Substitution takes place initially at the 1-position, a second substituent attacking the 8- and to a smaller extent the 6-position. Oxidation of pyrene gives a mixture of the 1,8- and 1,6-quinones in a proportion of about two to one; the former is more readily reduced by alkaline hydrosulfite and can thus be separated. 1-Hydroxypyrene and the 1,6- and 1,8-dihydroxypyrenes do not couple with diazonium salts, and on the basis of these reactions Fieser[7] has suggested that the structure (A), containing three benzenoid rings, makes the major contribution to the resonance of the pyrene molecule; structure (B), containing two benzenoid rings, makes a small contribution, but it is relatively stabilized in 1,6-dihydroxypyrene by the influence of the hydroxyl groups on the quinonoid system. With alkaline oxidizing agents pyrenequinone yields naphthalenetetracarboxylic acid,[8] an intermediate from which several important vat dyes are made. The acid may also be obtained by oxidizing the quinones resulting from sulfuric acid treatment of di-, tri- or tetrachloropyrenes.[9] 3,5,8,10-Tetrachloropyrene-1,6-quinone, which has no vat dyeing properties, may be condensed with ammonia or amines to yield blue to blue-green dyes.[10] Violet to black vat dyes of unknown constitution are obtained when tetrachloropyrene is heated with sodium-aluminum chloride at 130° and the product treated with sulfuric or nitric acid.[11]



A synthesis of 4,5,9,10-dibenzopyrene from 2-acetamidodiphenyl is to nitrate, hydrolyse, diazotize and treat with potassium iodide to give 2-iodo-3-nitrodiphenyl, converted by copper powder into 2,2′-dinitro-6,6′-diphenyldiphenyl, which is reduced, diazotized and cyclized by heat.[12]

[7] Fieser and Fieser, Organic Chemistry, 2nd ed., Heath and Co., Boston, 1950.

[8] Rütgerswerke, DRP Anm. R. 87,820; 87,822.

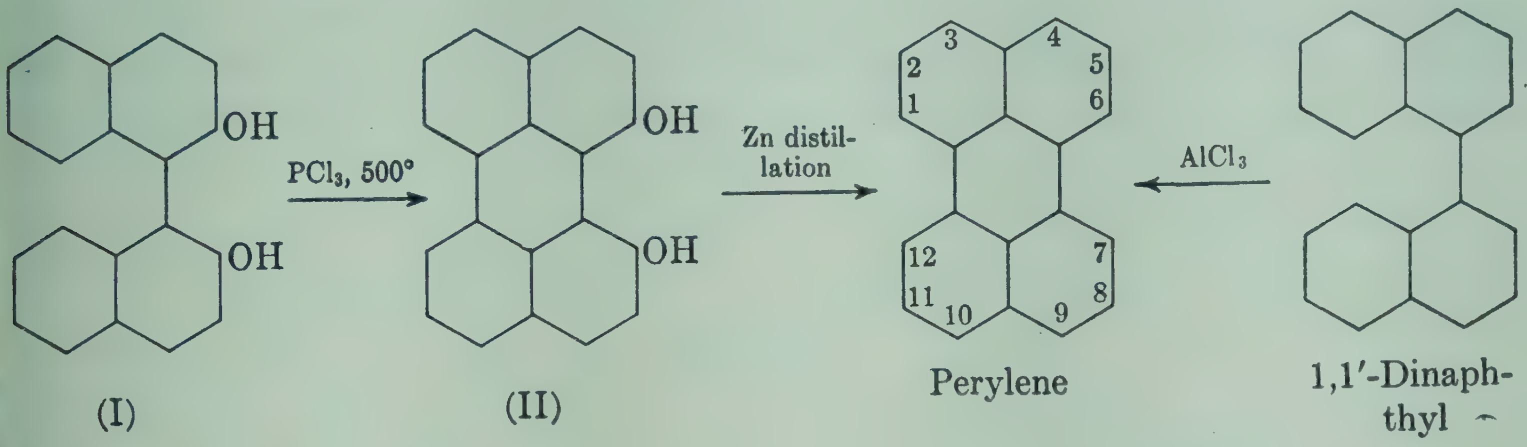
[9] IG, BP 421,813.

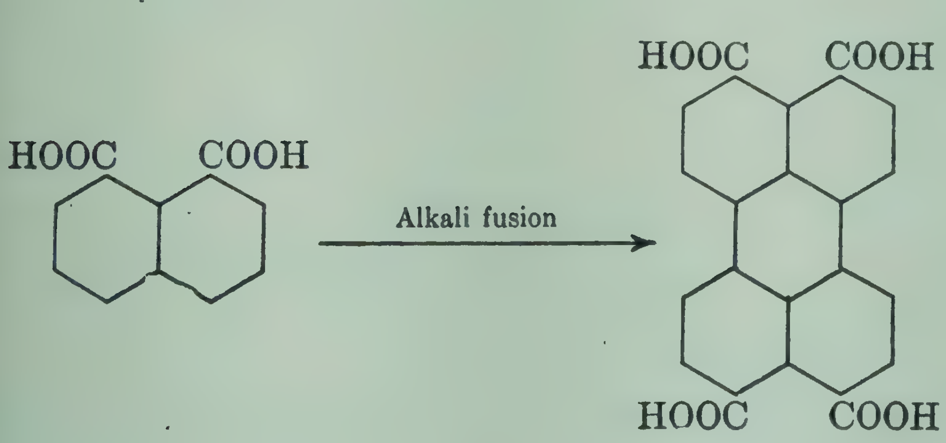
[10] IG, BP 434,027.

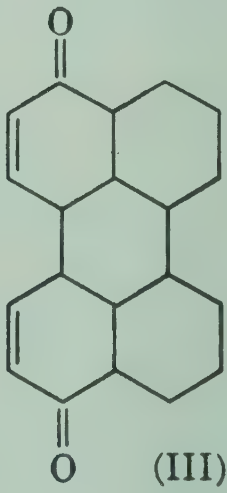
[11] Scholl and Meyer, SP 174,078.

[12] Sako, *Bull. Chem. Soc. Japan* **9,** 55 (1934).

Perylene.[13] Perylene (yellow leaflets, m.p. 273–4°) has not been isolated from nature. It is formed by the action of aluminum chloride on naphthalene or 1,1′-dinaphthyl;[14] or by the action of copper on 8,8′-diiodo-1,1′-dinaphthyl. A technically feasible method of preparation is from di-β-naphthol (I), which is obtained in excellent yield by oxidation of β-naphthol with ferric chloride; (I) may be converted into 1,12-dihydroxyperylene (II) by heating with phosphorus trichloride at 500°,[15] or with aluminum chloride and sodium carbonate at 150–170° (Zincke and Pereira).[13] Zinc dust distillation of (II) then gives perylene.[16] Perylene can also be prepared from (I) in one operation by heating with a mixture of phosphorus pentachloride and phosphorous acid and distilling off the hydrocarbon at about 600°. An interesting synthesis of perylene is by the action of aluminum chloride on 2,2′-dinaphthyl (made by dehydrogenation of naphthalene); a migration to the 1,1′-isomer has to be assumed as an intermediate stage.[17] Perylene can be obtained satisfactorily from the mixed dinaphthyls obtained by passing naphthalene vapors at 800° over a tungstic acid-aluminum oxide catalyst.[18]







(III)

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[13] See Mason, *Ind. Chemist* **5,** 111 (1929).

[14] Scholl, Seer, and Weizenböck, *Ber.* **43,** 2202 (1910).

[15] Hansgirg, DRP 386,040.

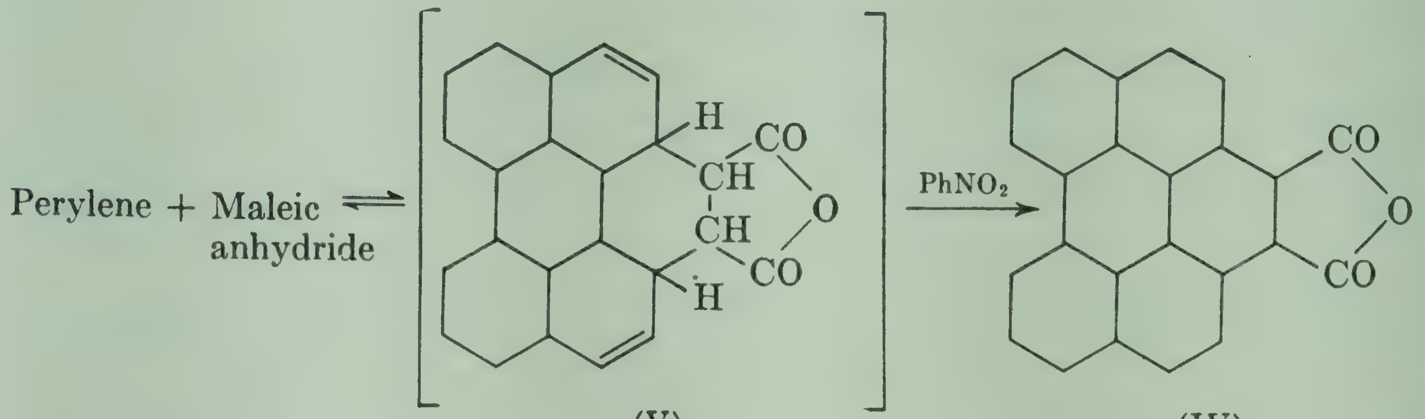
[16] See also Corbellini and Aymar, *Giorn. chim. ind. applicata* **10,** 196 (1928).

[17] IG, BP 425,363.

[18] IG, BP 445,896; see also BP 356,189; Orchin, USP 2,478,205.

Perylene-3,4,9,10-tetracarboxylic acid, obtained in excellent yield by the alkali fusion of naphthalene-1,8-dicarboxylic acid or its imide, is an intermediate from which some important vat dyes are prepared.

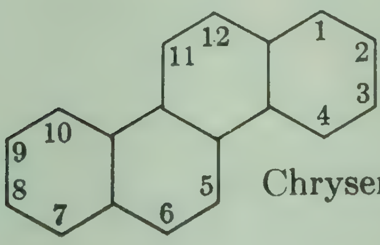
Initial attack of the perylene molecule in substitution reactions is in the 3-position, and further substitution occurs in the 10-, and to a smaller extent in the 9-position. Oxidation gives the 3,10-quinone (III) which dyes cotton yellow from a red vat. Perylene does not undergo the Diels-Alder reaction with maleic anhydride under ordinary conditions, but in boiling nitrobenzene the orange colored 1,12-benzoperylenedicarboxylic anhydride (IV) is formed; apparently, the adduct (V) is unstable and nitrobenzene prevents its dissociation by oxidizing it to (IV).



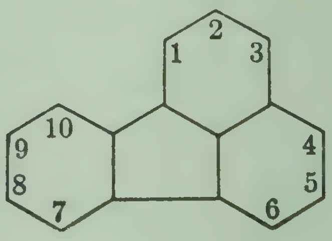
(V) (IV)

Isodibenzanthrone can be synthesized from perylene as starting material (*vide infra*), but the use of perylene for the commercial preparation of isodibenzanthrone or other vat dyes has not yet been established.

Chrysene (colorless rhombic plates, m.p. 255°). IG have a series of patents[19] on derivatives of chrysene, a minor coal-tar hydrocarbon of which few derivatives of proved constitution were known until recently, other than the 5,6- and 6,12-quinones. Chrysene can be prepared in 60% yield by the pyrolysis of indene, and methods for its synthesis from benzene, naphthalene and phenanthrene have been developed.



Chrysene



Fluoranthene

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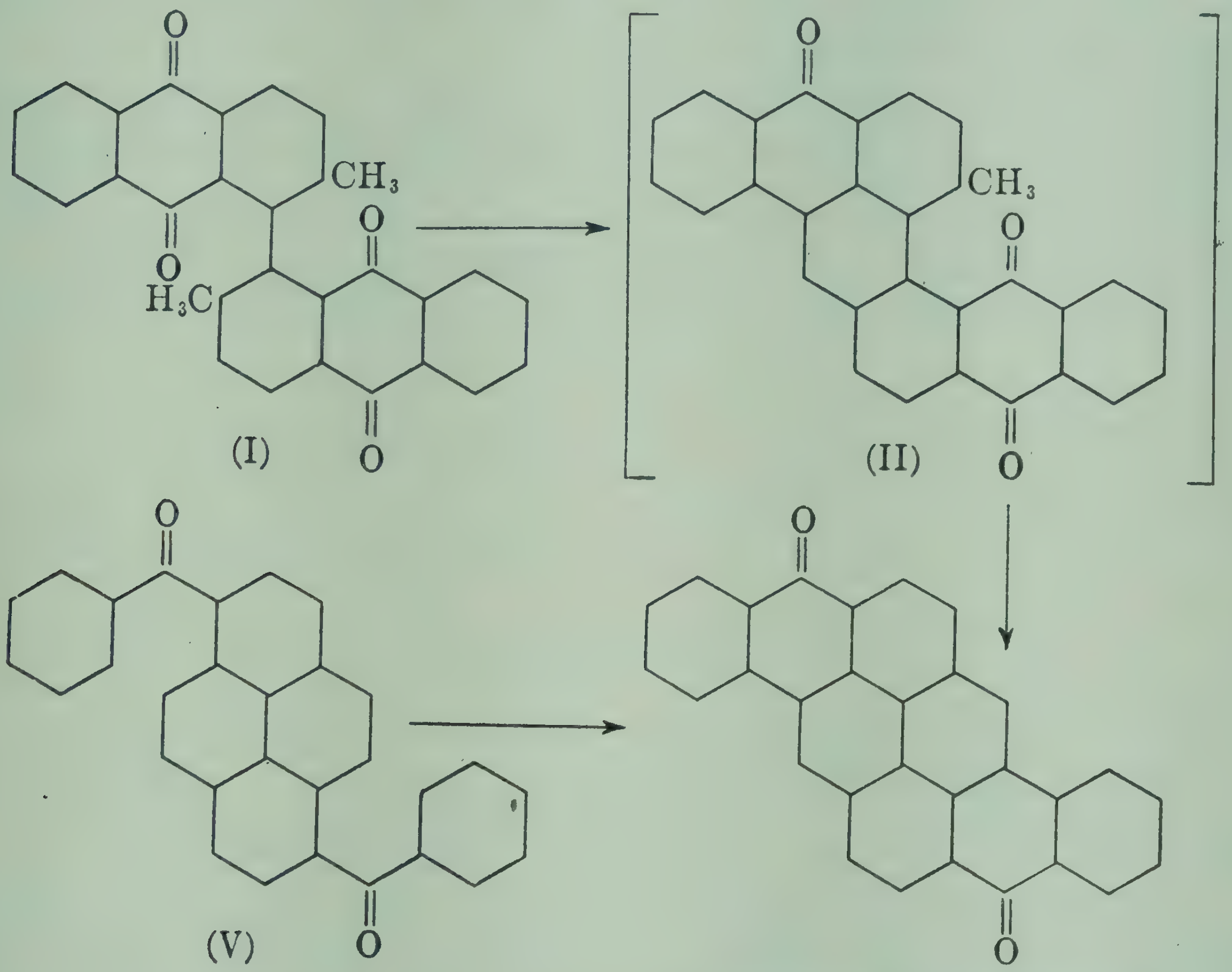
[19] IG, BP 438,609; 446,968; 449,182; 450,498; Ciba BP 427,236; cf. Funke, Müller and Vadasz, *J. prakt. Chem.* **144**(ii), 242 (1936); cf. also Funke and Ristic, *ibid.* **145**(ii), 309 (1936). For examples of vat dyes from chrysene, see Ciba, SP 218,368; 222,462–72.

Fluoranthene (colorless needles or plates, m.p. 109°). Ciba have several patents on the preparation of intermediates and dyes from fluoranthene,[20] another minor constituent of coal tar.[21]

PYRANTHRONES

Pyranthrone (Indanthrene Golden Orange G) (CI 1096) was discovered by Scholl (1905) in the course of his work on the constitution of flavanthrone; historically pyranthrone should therefore follow its nitrogen analog, flavanthrone, although in a systematic classification the carbocyclic compound takes precedence. When 2,2′-dimethyl-1,1′-dianthraquinonyl (I), which may be prepared by the action of copper on 1-chloro-2-methylanthraquinone, is fused with caustic potash, pyranthrone is formed.[22] 1-Bromo-2-methylanthraquinone, prepared in nearly quantitative yield by bromination of 2-methylanthraquinone in oleum-chlorosulfonic acid in presence of sulfuryl chloride,[23] is converted into (I) by



Indanthrene Golden Orange G

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[20] Ciba, BP 529,653; 533,962–3. See also DRP 633,821; BP 378,476. For examples of vat dyes from rubicene, coronene, etc., see IG, DRP 656,554; Ciba, FP 859,494; General Aniline and Film, USP 2,210,041; IG, DRP 650,058.

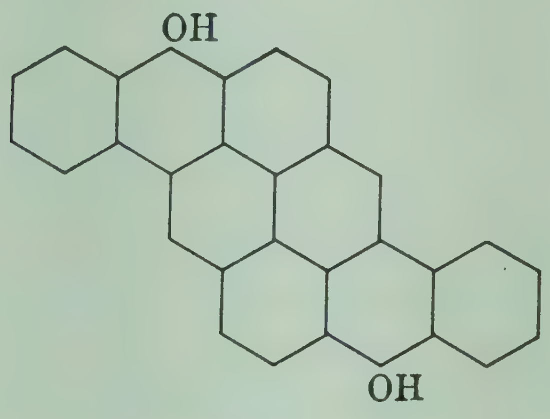
[21] For syntheses of fluoranthene and its derivatives, see Bergmann and Orchin, *JACS* **71,** 1917 (1949); Campbell, Wang and Gow, *JCS* 1513, 1555 (**1949**); Tucker, *ibid.* 2182; 3213; Kloetzel and Mertel, *JACS* **72,** 4786 (1950).

[22] Scholl, *Ber.* **43,** 346 (1910); **44,** 1448 (1911).

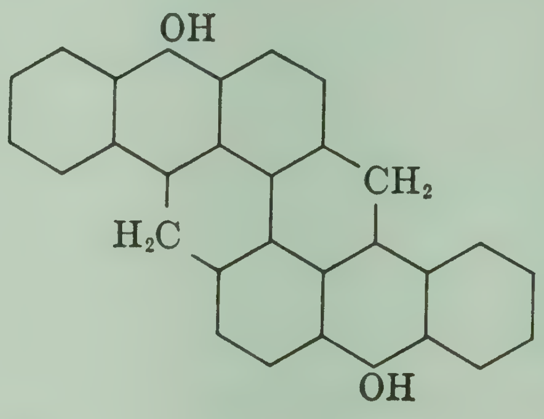
[23] Deinet, Gottlieb, and du Pont, USP 2,396,989.

heating with copper in naphthalene at 215°. The intermediate stage in the formation of pyranthrone from (I) is the yellow dye (II), which may be isolated by heating (I) with caustic potash at 75–80° in an organic diluent.[24] In the IG process[2] for Indanthrene Golden Orange G, 1-chloro-2-methylanthraquinone (416 kg.), *o*-dichlorobenzene (40), copper bronze (225) and pyridine (135) are heated at 150–160° for 3 hours; more *o*-dichlorobenzene (1150) and sodium carbonate (200) are added, and boiling continued for 3 hours. The product (I) is filtered off (316 kg.; 88% theory), and freed from copper by heating with dilute hydrochloric acid and sodium chlorate. Cyclization to pyranthrone is effected by refluxing (I) (150 kg.), caustic potash (81) and isobutyl alcohol (576) for 3 hours. The dye, recovered by adding water and distilling off the solvent, may be purified by a hypochlorite treatment (yield 152 kg. corresponding to 138 kg. of pure dye).

Pyranthrone requires only two equivalents of sodium hydrosulfite to form the crimson vat, and leucopyranthrone requires only two equivalents of an oxidizing agent for reoxidation. Leucopyranthrone is therefore the dihydro compound (III), and not the tetrahydro compound (IV) as postulated by Scholl. The purple colored vat changes to brown by further reduction in methyl alcoholic potassium hydroxide and (IV) may be ultimately formed.[25] Indanthrene Golden Orange G dyes brilliant orange shades with good fastness to light (5–6) and excellent fastness (4–5) to other agencies, but it is a powerful tenderer and exposure to direct sunlight has to be avoided both during and after dyeing.



(III)



(IV)

Besides being an anthrone derivative, pyranthrone contains the benzanthrone and the pyrene ring systems. Scholl demonstrated the relationship to pyrene, as well as the constitution of pyranthrone, by baking 1,6-dibenzoylpyrene (V) with aluminum chloride when pyranthrone was formed. The yield is improved by using air or manganese dioxide to facilitate dehydrogenation. Toluoyl- and chlorobenzoylpyrenes yield orange dyes.[26] Scholl's synthesis has now become a technical possibility, since coal-tar pyrene has become available. Further, the Scholl cyclization with aluminum chloride has proved to be a valuable method for determining the constitution of the complex dyes of the polycarbocyclic quinone class, and to be a technically feasible method of preparation for several dyes.[27]

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[24] IG, BP 360,102.

[25] Appleton and Geake, *Trans. Faraday Soc.* **37**, 45 (1941).

Bromination of pyranthrone in chlorosulfonic acid at about 60° in presence of a little sulfur gives the dibromo compound, Indanthrene Orange RRT (formerly RT), or the tribromo compound, Indanthrene Orange 4R (ST Erg. II 1246) (Caledon Brilliant Orange 4R), according to the proportion of bromine employed. The tribromo compound as obtained by the bromination process is somewhat yellower than the type, and the true shade is produced by a hypochlorite treatment. The bromine atoms are in α-positions.[4a] A brominated pyranthrone was formerly marketed as Indanthrene Scarlet G (CI 1098), and a chlorinated pyranthrone as Indanthrene Golden Orange R (CI 1097). Brominated pyranthrones containing 35–44% bromine and giving clearer vats are obtained if the bromination is carried out in chlorosulfonic acid in presence of a halogenating catalyst and a compound of boron.[28] Bromination can be continued to form the tetrabromo compound (Br 44.3%), which is not marketed, but used by IG as an intermediate for the preparation of Indanthrene Direct Black RB (see later).

Dibenzopyrenequinones

Dyes of this group are valued in calico printing for their ready vatting and reoxidation. Two types of dibenzopyrenequinones have been used as dyes, 2,3,7,8-dibenzopyrene-1,6-quinone and 2,3,6,7-dibenzopyrene-1,8-quinone, but the second type has little practical interest now. Indanthrene Golden Yellow GK may be prepared by an application of the Scholl cyclization with aluminum chloride to 3-benzoylbenzanthrone (I) or to 1,5-dibenzoylnaphthalene (II).[29] The Friedel-Crafts reaction between benzanthrone and benzoyl chloride yields (I), and the position taken up by the benzoyl group, from which the constitution of the dye follows, is clear from the general reactivity of benzanthrone in the 3-position in the first instance; thus mononitration gives the 3-nitro compound which can be converted into (I) through the amine, nitrile and carboxylic

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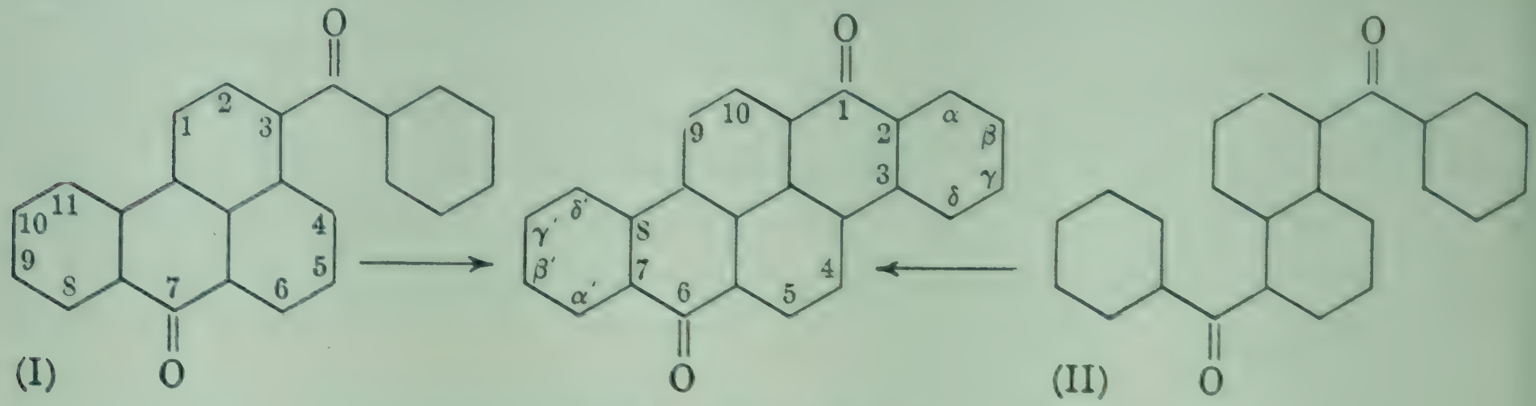
[26] IG, BP 382,877.

[27] Scholl and Seer, *Ann.* **394,** 143 (1912); **398,** 82 (1913).

[28] Fleysher, Ogilvie and National Aniline, USP 2,074,381.

[29] MLB, DRP 412,053; 423,283; 426,710.



Indanthrene Golden
Yellow GK

acid, and condensation of the acid chloride with benzene.[30] The Friedel-Crafts reaction between benzanthrone and benzoyl chloride, and dehydrogenation to Indanthrene Golden Yellow GK, may be carried out in one operation by using excess of aluminum chloride. The second stage is facilitated by the addition of oxidizing agents (e.g. manganese dioxide or *m*-nitrobenzenesulfonic acid),[31] or by passing oxygen or chlorine into the melt (Mayer and Wolfram, 1923). The IG process[4a] starts from 1,5-dibenzoylnaphthalene (II), which is obtained in a yield of about 46% by heating naphthalene (263 kg.), benzoyl chloride (770 kg.) and aluminum chloride (1100 kg.) at 70° for 8 hours.[31a] After treatment with water, the ketone is filtered off and crystallized from chlorobenzene; the product contains about 3% of 1,8-dibenzoylnaphthalene. The next stage is to melt aluminum chloride (1600 kg.) and common salt (385 kg.) at 110° and add (II) (375 kg.) in portions while passing in oxygen. Nitrogen is introduced above the melt at about four times the rate of oxygen. The temperature rises to 160° and the reaction is complete in 2–3 hours. After removal of aluminum salts with dilute hydrochloric acid, the dye is purified by vatting and reoxidation and a hypochlorite treatment. The dibromo derivative of Indanthrene Golden Yellow GK is the redder RK brand (Kränzlein, Sedlmayr, and Vollmann, 1924). Bromination is effected by the addition of bromine to the ketone-aluminum chloride melt at 150–155° during 20 hours.[2] Indanthrene Golden Yellow GK and RK give bordeaux colored vats, and the shades are brighter and faster than those from flavanthrone. Because of the beauty of the shades, these are important dyes. The fastness grades of Yellow GK are light 5–6, chlorine 5 and soda-boil 2–3; the light fastness is increased to 6–7 and the soda-boil fastness to 3–4 in the dibromo derivative. Both the dyes are moderately active as light-tenderers, the halogenated dye being less active. Indanthrene Golden Yellow GK pasted with the aid of glycerine is marketed as Indanthrene Printing Yellow GOK Suprafix.[3] Indanthrene Printing Yellow GOW, which has improved fastness to washing, is a bromodichloro compound prepared by the halogenation of Indanthrene Golden Yellow GK in chlorosulfonic acid.[3] A mixture of Indanthrene Golden Yellow RK (5.95 parts), violanthrone (2.47) and Indanthrene Bordeaux RR (3.95), converted into a Suprafix type of paste, is sold as Indanthrene Brown TM for printing.[3]

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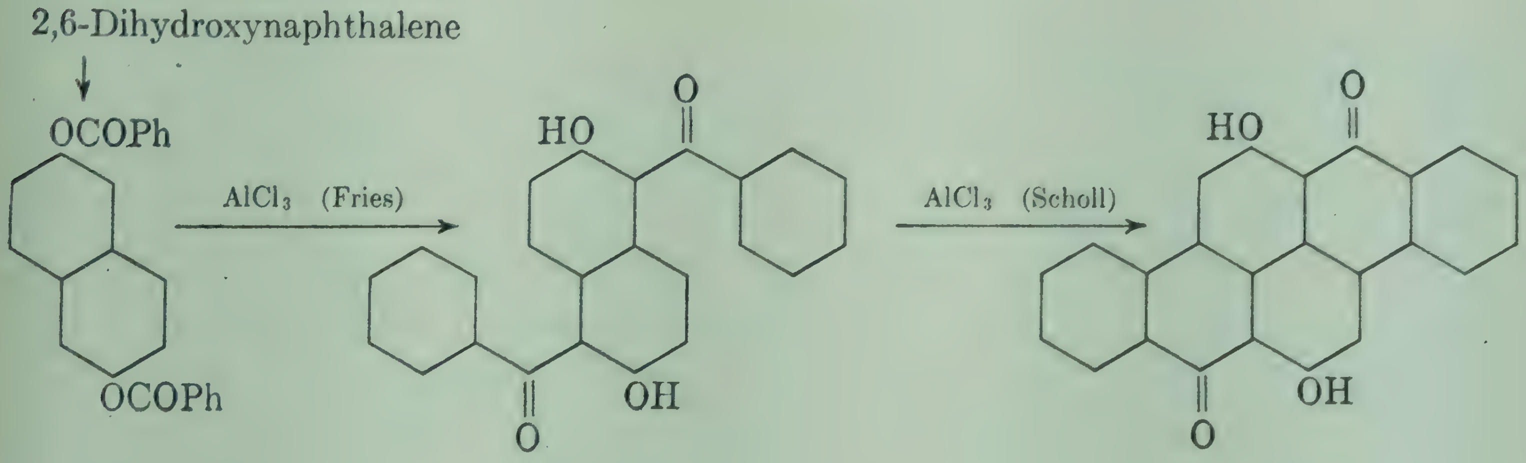
[30] According to Moschtschinskaja, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 1376 (1939), benzanthrone reacts with benzoyl chloride and aluminum chloride to give a mixture of 2- and 3-benzoylbenzanthrone; but the proportion of the isomerides is not mentioned.

[31] Ciba, BP 501,897; USP 2,238,180.

[31a] See also IG, DRP 576,253.

Kunz[6] has made a careful study of the bromination of Indanthrene Golden Yellow GK, and has shown the influence of the conditions of the reaction on the orientation of the halogen atoms, which in turn affects the shade and the fastness. Halogenation in an organic solvent requires a carrier, such as iodine, and the bromine atoms enter the β,β'-positions; the shades are redder and faster than those from the parent compound. Halogenation in chlorosulfonic acid in presence of iodine proceeds similarly, but in oleum in the absence of a carrier the γ,γ'-dibromo compound is formed, which dyes more greenish and less fast shades. Halogenated dibenzopyrenequinones can also be prepared by the cyclization of 3-benzoylbenzanthrones containing halogen atoms in the benzene or benzanthrone residues.[32]

Dihydroxy and dimethoxy derivatives of Indanthrene Golden Yellow GK can be readily prepared from 2,6-dihydroxynaphthalene as indicated.[33]



2,3,6,7-Dibenzopyrene-1,8-quinone (III) is prepared by the Scholl reaction on 4-benzoylbenzanthrone (IV) or on 1,4-dibenzoylnaphthalene (V).[34] This red dye is not useful; the dibromo compound, Indanthrene

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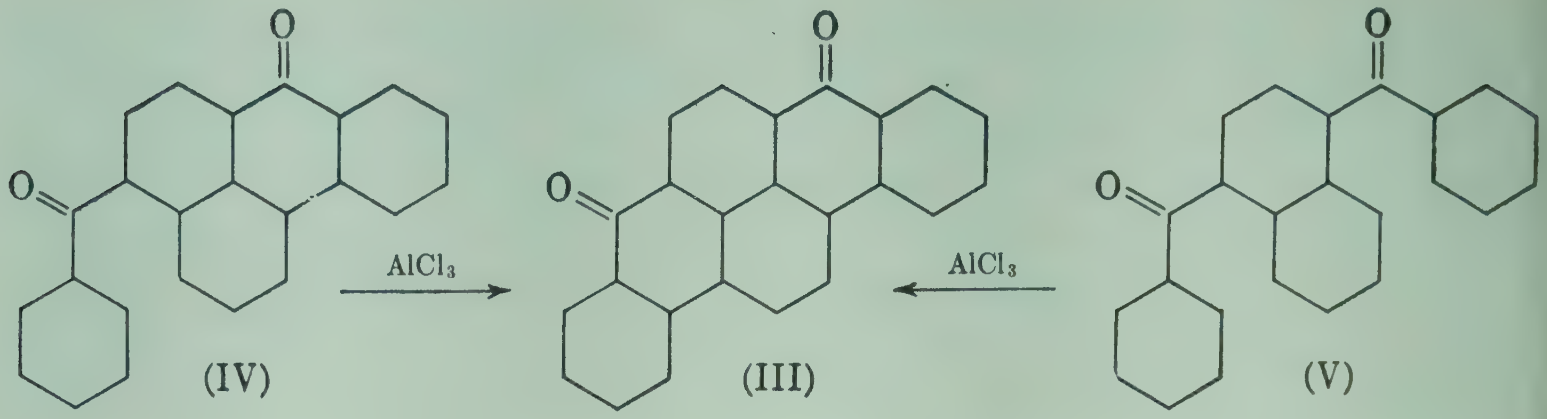
[32] Braun and IG, DRP 742,811.

[33] IG, DRP 453,280; 455,955.

[34] IG, DRP 542,800; Scholl and Newmann, *Ber.* **55**, 118 (1922).



Scarlet 4G (Kränzlein, 1927), was marketed, but it has also failed to find a permanent place in the commercial range.

The pyrenequinone series of dyes can be extended by the condensation of the halogenated compounds with aminoanthraquinones. Condensation of monoamino- and diaminodibenzopyrenequinones with benzoyl chloride or anthraquinone-2-carboxyl chloride gives red to violet dyes.[35] Dihydroxy derivatives are halogenated and/or alkylated for scarlet to violet dyes.[36] Phthaloylpyrenes are orange vat dyes, converted by the usual reactions into olive-green, brown and gray dyes.[37] A yellowish-orange dibenzopyrenequinone is made by alkaline condensation of benzanthrone and *o*-chlorobenzoic acid, followed by cyclization with acid.[38]

ANTHANTHRONES

Dehydration of 1,1′-dinaphthyl-8,8′-dicarboxylic acid (I) by means of sulfuric acid results in cyclization to the orange anthanthrone,[39] which has vat dyeing properties, but is of no practical value in view of its poor tinctorial power. The dichloro and dibromo compounds, however, are valuable dyes (Indanthrene Brilliant Orange GK and RK) (ST Erg. II 1286b) which are level dyeing; the bright attractive orange shades (from a red-violet vat) have light fastness 7–8, chlorine fastness 5, and soda-boil fastness 3–4. The light-tendering activity is low. The technical synthesis[2] of anthanthrone (Chart 2) starts from peri-acid and involves a number of stages, but they proceed in good yields. Cyclization of (I) to anthanthrone and bromination can be effected simultaneously by dissolving (I) in a mixture of monohydrate and oleum, adding bromine and a little phosphorus, and heating at 65° for a few hours. The bromine atoms probably enter the starred positions. Indanthrene Brilliant Orange GK is prepared by cyclizing (I) with 96% sulfuric acid at 50° and passing chlorine into the solution in presence of a little ferrous sulfate.

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[35] IG, BP 307,926; 338,882; 358,502; 358,509.

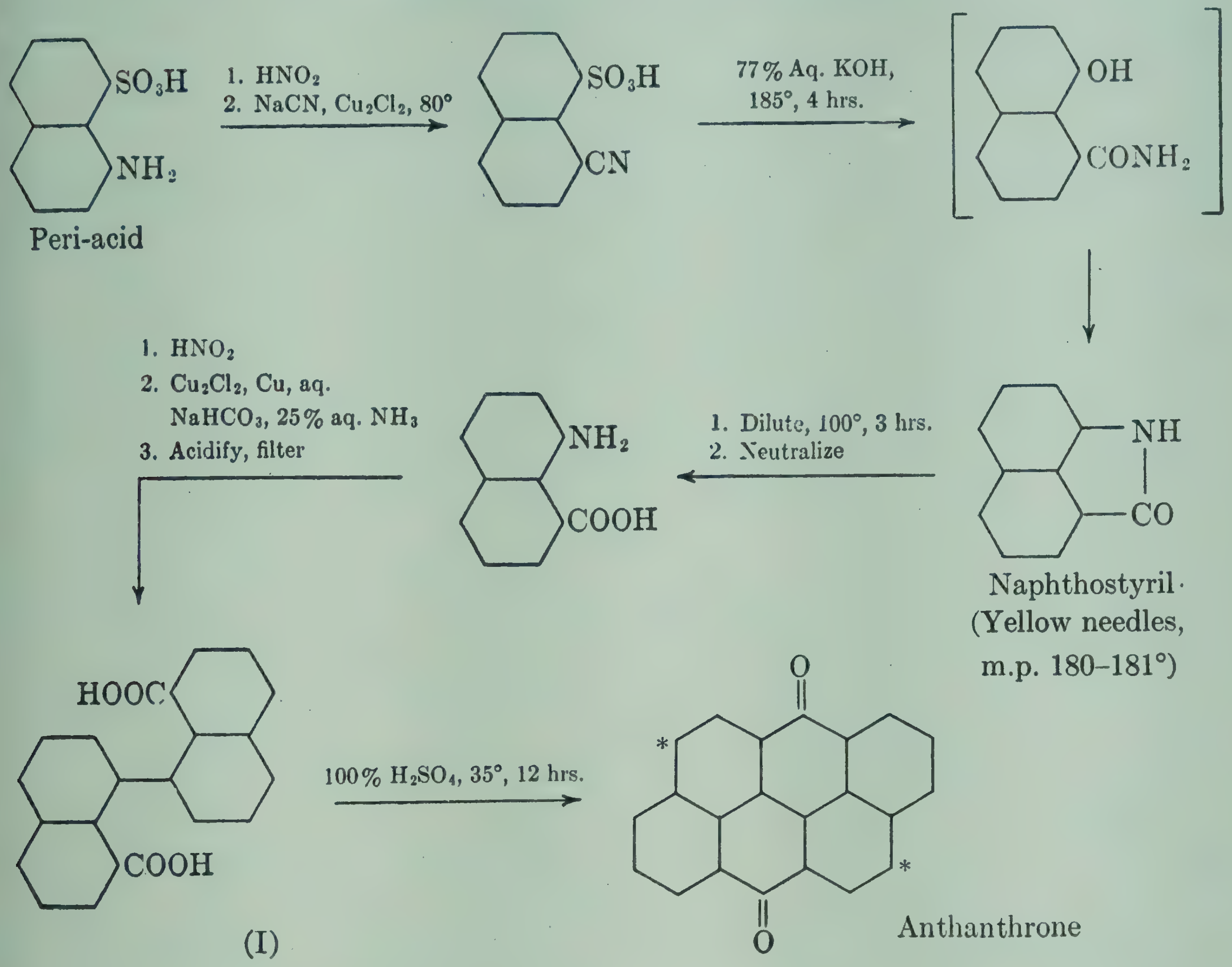
[36] IG, BP 360,215.

[37] Sedlmayr, BP 366,472.

[38] Thomson, Carter, Thomas, and ICI, BP 358,426.

[39] Kalb, *Ber.* **47,** 1724 (1914); DRP 280,787; Cassella, DRP 459,404; 441,225; 444,325; 452,063.

CHART 2
PREPARATION OF ANTHANTHRONE


SO_3H
NH_2
Peri-acid
1. HNO_2
2. NaCN, Cu_2Cl_2, 80°
SO_3H
CN
77% Aq. KOH, 185°, 4 hrs.
OH
$CONH_2$
NH
CO
Naphthostyril
(Yellow needles, m.p. 180–181°)
1. Dilute, 100°, 3 hrs.
2. Neutralize
NH_2
COOH
1. HNO_2
2. Cu_2Cl_2, Cu, aq. $NaHCO_3$, 25% aq. NH_3
3. Acidify, filter
HOOC
COOH
(I)
100% H_2SO_4, 35°, 12 hrs.
O
O
*
*
Anthanthrone

Indanthrene Scarlet RM is a mixed bromo-iodo derivative of anthanthrone, used mainly for shading Indanthrene Brilliant Orange RK and prepared by heating the latter with (I), arsenic acid and iodine in sulfuric acid. Indanthrene Scarlet GK is a mixture of Indanthrene Brilliant Orange RK (60) and Indanthrene Scarlet RM (40).[2]

The anthanthrone type has useful properties and a series of dyes produced by the introduction of amino, acylamido, anthraquinonylamino and other groups have been described in the patent literature.[40] Indanthrene Grey BG is the condensation product of dibromoanthanthrone with 1-amino-4-benzamidoanthraquinone (2 moles).[3] Blue to gray dyes are produced by condensing a dihalogenoanthanthrone with one mole each of α-aminoanthraquinone and an aminoaroylamidoanthraquinone.[41]

Anthanthrone fused with aqueous potassium hydroxide, potassium chlorate and a little copper yields a dihydroxyanthanthrone which may be alkylated. The oxidizing agent is not essential, but its use prevents the formation of the dihydro derivative.[42] Nitration and reduction of naphthalene-1,4-dicarboxylic acid give naphthostyril-5-carboxylic acid, from which 1,1′-dinaphthyl-5,8,5′,8′-tetracarboxylic acid and anthanthrone-3,8-dicarboxylic acid can be prepared; the last is a useful dye intermediate.[43]

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[40] E.g. IG, DRP 485,961; 487,023; 507,343; Slinger and ICI, BP 633,499.

[41] Zerweck, Müller, Bähr, and General Aniline and Film, USP 2,320,694.

BENZANTHRONE DERIVATIVES

The benzanthrone dyes constitute an extremely important group which includes some of the fastest and most widely used dyes in the entire vat dyes range. Bally (1904) observed that when β-aminoanthraquinone was treated with glycerol and sulfuric acid in the absence of an oxidizing agent, such as nitrobenzene, the formation of a pyridine ring was accompanied by the formation of an additional benzene ring, and the product was "benzanthronequinoline" (9[*N*],8-pyridinobenzanthrone; see later) instead of 5,6-phthaloylquinoline, which he had expected.[44] Condensation of two moles of acrolein with one of β-aminoanthraquinone had therefore taken place, and it was then found that the condensation of anthrone (or anthranol), glycerol and sulfuric acid gave benzanthrone. Scholl confirmed the constitution of benzanthrone by cyclizing 1-benzoylnaphthalene to benzanthrone by means of aluminum chloride. Alkali fusion of benzanthrone gave a blue dye, dibenzanthrone (violanthrone; CI 1099), by the union of two benzanthrone nuclei in the 3,3′- and 4,4′-positions; and alcoholic alkali fusion of 3-chlorobenzanthrone gave the isomeric isodibenzanthrone (isoviolanthrone), a violet dye. A series of important dyes have been obtained by halogenation, nitration and the introduction of methoxyl groups. The shades of the dyes in this group are violet, blue, green, olive, and black. The vats exhaust rapidly and for avoiding unlevel shades, especially when dyeing the violets and greens and when dyeing pale shades generally, the addition of a retarding agent (e.g., glue or sulfite cellulose liquor) is useful. The fastness properties are good to excellent (light 5–8, chlorine 4–5, soda-boil 3–4). Water-spotting and hot-pressing cause a temporary change of shade, particularly of the violets.

In preparing benzanthrone[2,45] from anthraquinone it is not necessary to isolate anthrone. To a mixture of 96% sulfuric acid (2100 kg.), water (200) and anthraquinone (300) at 125°, iron powder (228) and glycerol

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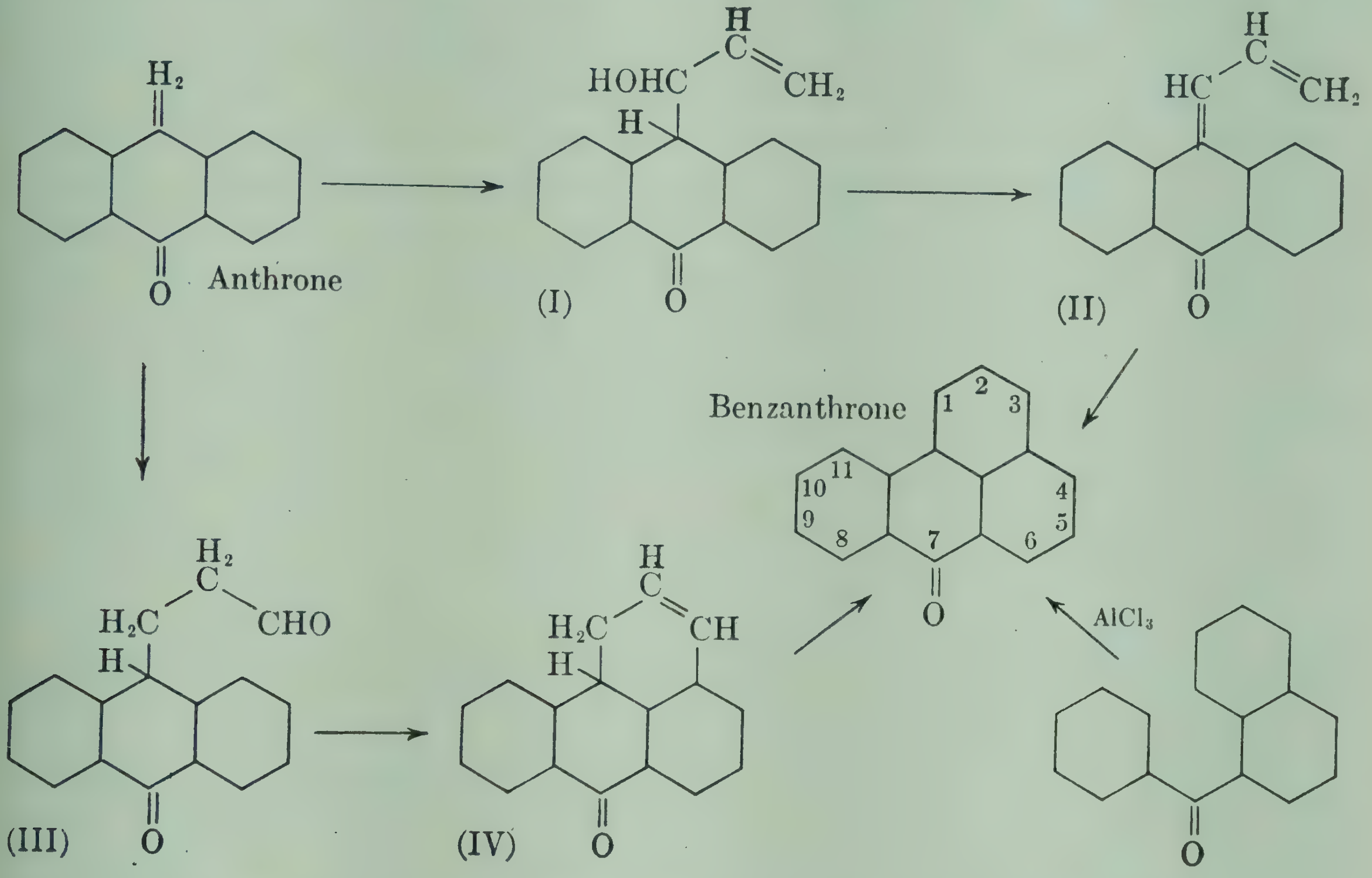
[42] Corbellini and Crespi, *Rend. ist. lombardo Sci.* (2) **69,** 580 (1936).

[43] Stilmar and du Pont, USP 2,292,551.

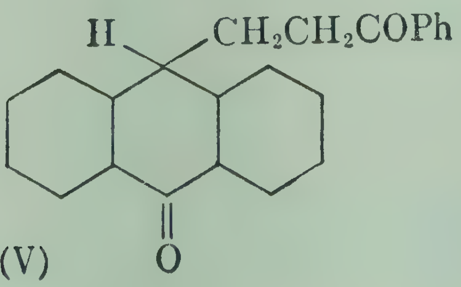
[44] *Ber.* **38,** 194 (1905); Bally and Scholl, *Ber.* **44,** 1656 (1911).

[45] Macleod and Allen, *OSCV* II, p. 62. See also Lukin, *J. Gen. Chem.* (*U.S.S.R.*) **18,** 308 (1948).

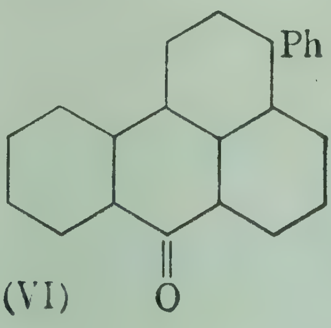
(166) are added; a vigorous exothermic reaction ensues, and the temperature is kept at 132–137° by cooling the reaction kettle. The reaction is complete in an hour, and on dilution with water the precipitated benzanthrone is collected, treated with caustic soda solution to remove alkali-soluble impurities, washed and dried (yield 335 kg. of 86% purity, or 288 kg. of 100%). Benzanthrone crystallizes readily in yellow needles, m.p. 170°, from acetic acid and other common solvents, but is best purified by vacuum distillation. The benzanthrone condensation is a general reaction and any α,β-unsaturated aldehyde, ketone or ketonic ester can be


H₂
O
Anthrone
H
C
HOHC
CH₂
H
(I)
O
H
C
HC
CH₂
(II)
O
Benzanthrone
1
2
3
4
5
6
7
8
9
10
11
O
H₂
C
H₂C
CHO
H
(III)
O
H
C
H₂C
CH
H
(IV)
O
AlCl₃
O

employed in place of acrolein.[46] The reaction may proceed through the aldol (I) and allylidene-anthrone (II) (Bally and Scholl); alternatively, the mechanism may be α,β-addition to acrolein to form (III), which cyclizes to dihydrobenzanthrone (IV) (Meerwein).[47] The Meerwein mechanism is supported by the formation of 3-methylbenzanthrone, and


H
CH₂CH₂COPh
O

(V)



(VI)

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[46] Cf. IG, DRP 482,839; 490,187; 499,050.

[47] *J. prakt. Chem.* **97**, 284 (1918).

not 1-methylbenzanthrone, from methyl vinyl ketone;[48] and by the isolation of the adduct (V) from anthrone and phenyl vinyl ketone as an intermediate in the formation of 3-phenylbenzanthrone (VI).[49] Baddar and Warren have found that in general α,β-unsaturated aldehydes and ketones react at the double bond with anthrone (Meerwein mechanism); but cinnamaldehyde, which is an exception, and aldehydes generated *in situ* from the corresponding glycerol, react at the aldehyde group (Bally-Scholl mechanism).[50] It has also been suggested that the aldehyde group first condenses at an α-position of anthrahydroquinone or oxanthrone and ring closure then follows, but the evidence is inconclusive. The α,γ-diethyl ethers of β-substituted glycerols can be used for the synthesis of 2-alkyl- and 2-arylbenzanthrones.[51] A method of synthesizing 2-chlorobenzanthrones is to condense anthrone or its halogen derivatives with α,β,γ,γ-tetrachloropropylene. The products include 2-chloro-, 2,6- and 2,8-dichloro-, 2,6,11- and 2,8,11-trichlorobenzanthrones.[52] Benzanthrene can be prepared together with dihydrobenzanthrene from 1-benzylnaphthalene by a vapor-phase dehydrogenation in presence of an inert vapor, using metallic oxides as catalyst.[53] Benzanthrene is oxidized to benzanthrone in good yields by the usual methods.[54]

By reduction of benzanthrone with a metal in presence of aluminum chloride and a solvent two distinct hydrocarbons have been isolated.[55] Benzanthrone can be oxidized to anthraquinone-1-aldehyde by treatment with ozonized air in glacial acetic acid;[56] and to anthraquinone-1-carboxylic acid by chromic acid oxidation. Halogenation and nitration of benzanthrone take place in the 3, and the 3,9-positions.[57, 58] Facile substitution in the 3-position is analogous to α-substitution in naphthalene, the benzene ring not deactivated by the carbonyl group being attacked. Monosulfonation, however, gives mainly the 9-sulfonic acid.[59] In the disubstitution reactions the diphenyl residue in benzanthrone comes into play.[60] The 4-position is attacked by aqueous potassium hydroxide and chlorate, yielding 4-hydroxybenzanthrone;[61] by caustic potash and aniline, yielding a small amount of 4-anilinobenzanthrone;[57] and by piperidine, sodamide and oxygen, giving a nearly theoretical yield of 4-piperidinobenzanthrone.[62] When benzanthrone in dimethylaniline is heated with sodamide and oxygen, the principal products are 6-aminobenzanthrone, 6-hydroxybenzanthrone and 6,6′-dibenzanthronylamine.[62] By the action of Grignard reagents on benzanthrone, 6-phenyl, benzyl and cyclohexylbenzanthrones have been prepared in good yield.[5, 63] 3-Acylbenzanthrones have been prepared by a Diels-Alder reaction between methyleneanthrone and α,β-ethynyl ketones, the addition being accompanied by oxidation.[64] Methyleneanthrone condenses with quinones to give condensed ring systems, behaving as a diene in a Diels-Alder reaction; with α-naphthoquinone the product is 2,3-phthaloylbenzanthrone, which is a yellow vat dye.[65] Methyleneanthrone (light yellow prisms, m.p. 148°) is obtained in nearly quantitative yield by treating anthrone and aqueous formaldehyde in boiling alcohol with a little piperidine.[66]

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[48] Mayer, *Künstliche Organische Farbstoffe*, Springer, Berlin, 1934, p. 184.

[49] Allen and Overbaugh, *JACS* **57,** 1322 (1935).

[50] Baddar and Warren, *JCS* 401 (1938); 944, 948 (1939).

[51] Baddar and Warren, *Nature* **140,** 321 (1937).

[52] Heilbron, Irving, and ICI, BP 447,546; Heilbron, Heslop, and Irving, *JCS* 781 (1936).

[53] IG, BP 409,770.

[54] IG, DRP Anm. J. 45,117.

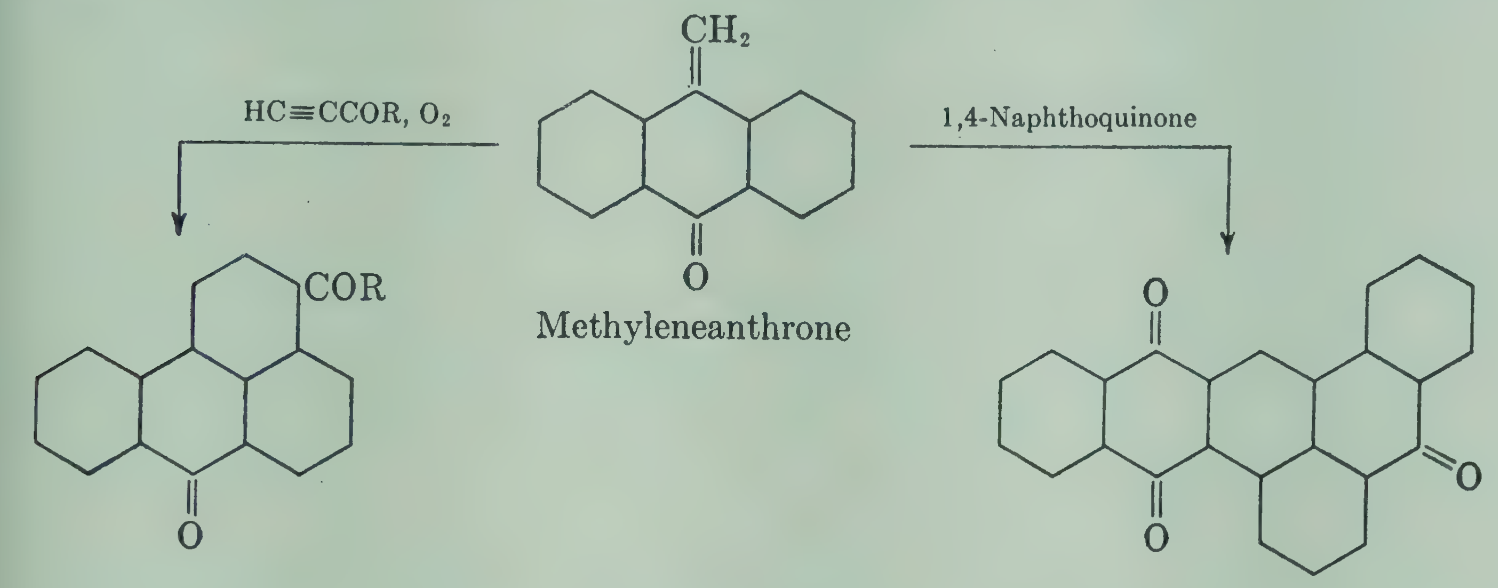
[55] Clar, DRP Anm. C. 48,124.

[56] IG, BP 472,167.

[57] Lüttringhaus and Neresheimer, *Ann.* **473,** 259 (1929).

[58] Cahn, Jones, and Simonsen, *JCS* 444 (**1933**); Liebermann and Roka, *Ber.* **41,** 1423 (1908); Maki and Nagai, *J. Soc. Chem. Ind. Japan* Suppl. Binding **38,** 487B (1935).

[59] Pritchard and Simonsen, *JCS* 2047 (**1938**).



Dibenzanthrones. The constitution of dibenzanthrone follows from the Scholl cyclization of 4,4′-dibenzoyl-1,1′-dinaphthyl (VII) to the dye;[67]

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[60] Maki, *J. Soc. Chem. Ind. Japan* **37,** 2198 (1934).

[61] Perkin and Spencer, *JCS* **121,** 479 (1922).

[62] Bradley and Robinson, *JCS* 1254 (**1932**); Bradley, *JCS* 1175 (**1948**) and earlier papers.

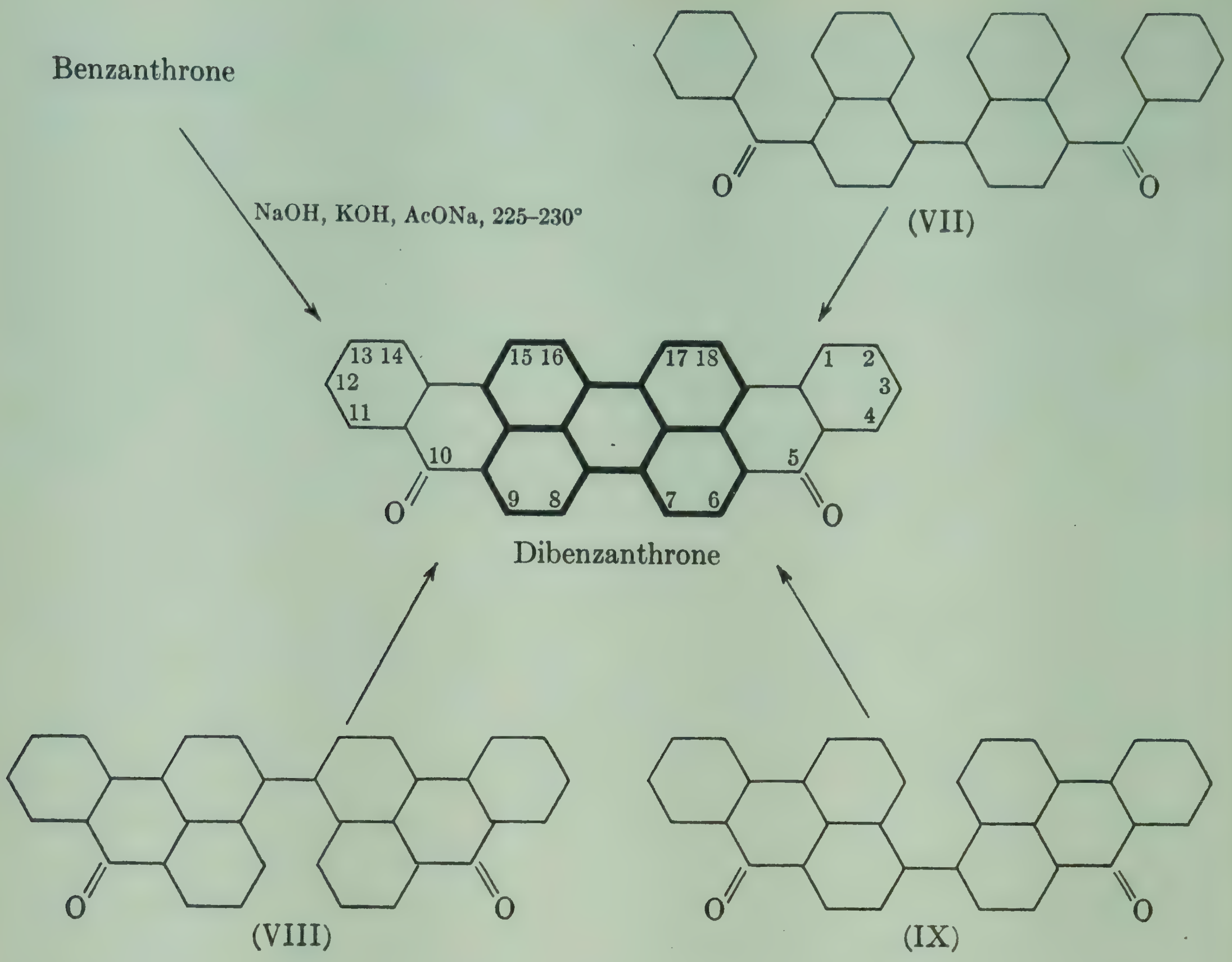
[63] Allen and Overbaugh, *JACS* **57,** 740 (1935); Charrier and Ghigi, *Ber.* **69,** 2211 (1936).

[64] Irving and Johnson, *JCS* 2037 (**1948**); see also Irving, Johnson, and ICI, BP 604,491.

[65] IG, BP 379,798.

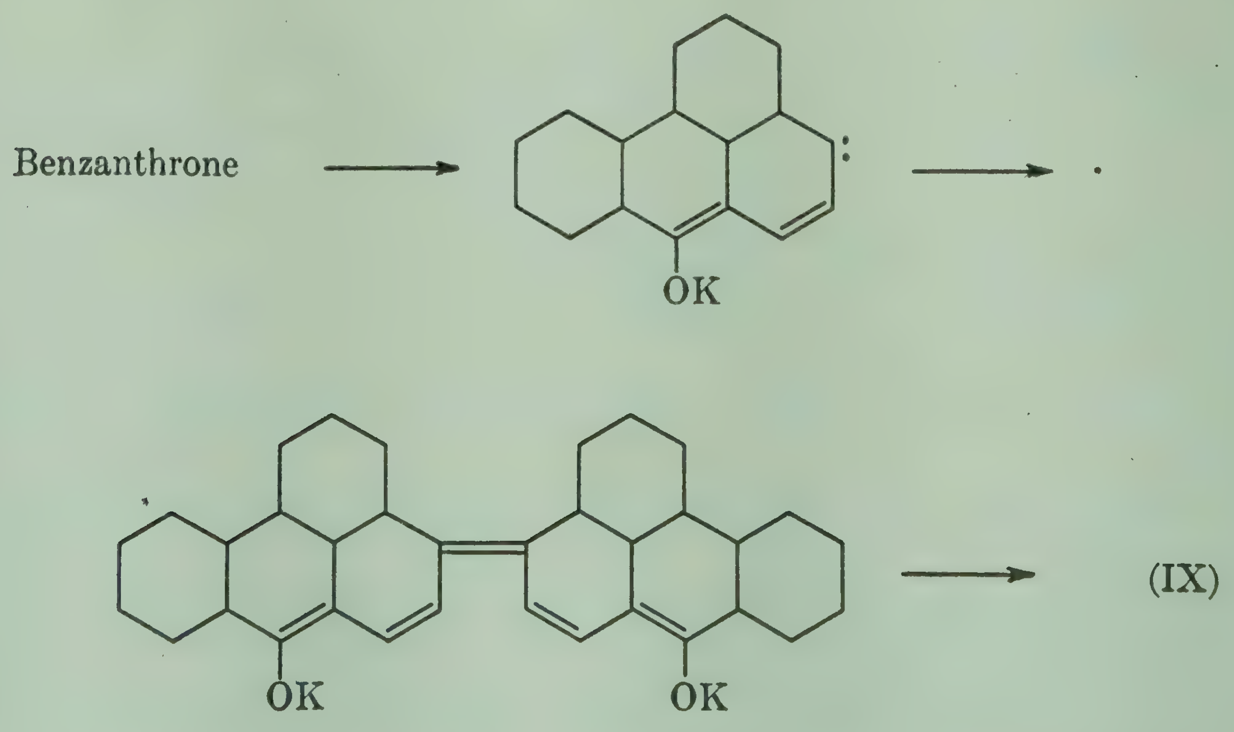
[66] Clar, *Ber.* **69,** 1687 (1936).

[67] Scholl and Seer, *Ann.* **394,** 129, 171 (1912).

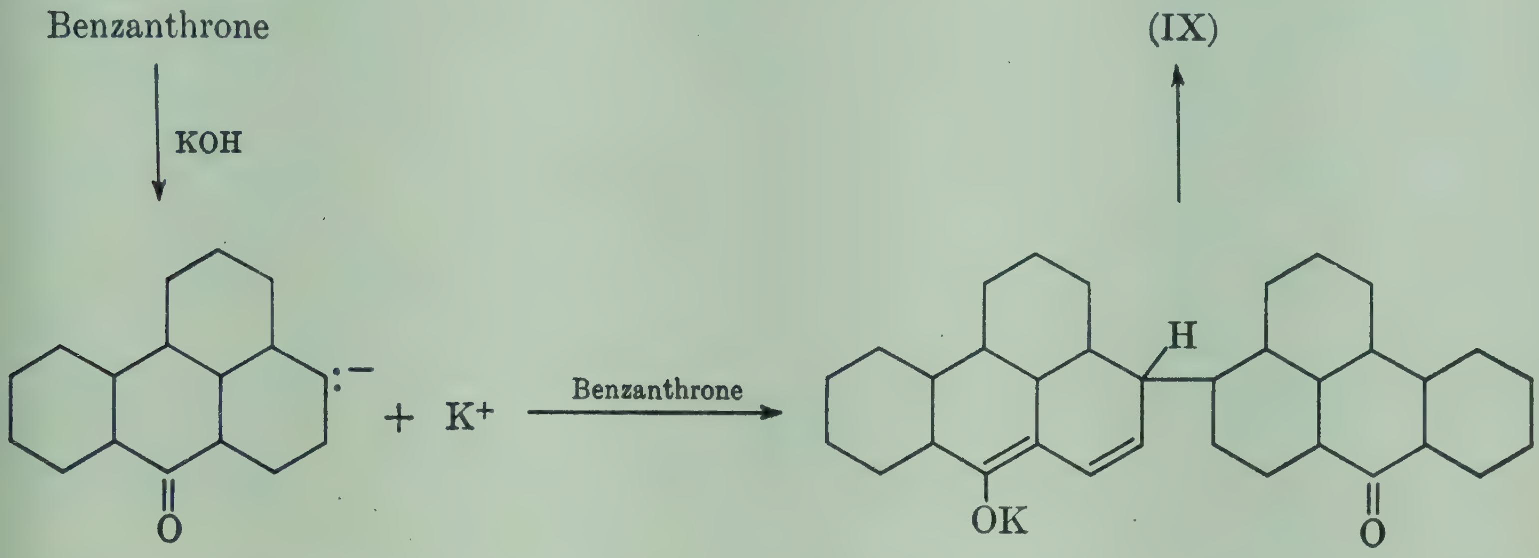

Benzanthrone
NaOH, KOH, AcONa, 225–230°
O
O
(VII)
13 14
12
11
10
15 16
9 8
17 18
7 6
1 2
3
4
5
O
O
Dibenzanthrone
O
O
(VIII)
O
O
(IX)

further, dibenzanthrone can be prepared by the alkali fusion of both 3,3′- and 4,4′-dibenzanthronyl (VIII and IX). The perylene ring system in dibenzanthrone is indicated in dark lines.

Lüttringhaus and Neresheimer[57] established that 4,4′-dibenzanthronyl (IX) is an intermediate stage in the formation of dibenzanthrone. They assumed that under the influence of strong alkali benzanthrone enolized to the indicated unsaturated residue, which dimerized to the dipotassium


Benzanthrone
OK
OK
OK
(IX)

salt of dihydro-4,4′-dibenzanthronyl, and the latter then underwent oxidation to 4,4′-dibenzanthronyl (IX). The activation of the 4-position in benzanthrone by alkali is shown by the fact that 3,3′-dibenzanthronyl (VIII) can be converted to dibenzanthrone under much milder conditions of alkali fusion than 4,4′-dibenzanthronyl. Bradley[67a] has suggested that, by analogy with the hydroxylation of benzanthrone which takes place by the attachment of an anion (hydroxyl) to benzanthrone when it is fused with alkali in the presence of an oxidant, the self-condensation of benzanthrone in presence of caustic potash is the result of an attack of benzanthrone by an anion of benzanthrone:



Violanthrone as now manufactured is much purer than the early representatives as a result of progressive improvements in methods of manufacture; the yield has also been greatly improved. The presence of a phenolic by-product in benzanthrone, which gave a homogeneous melt, was a necessary factor in the original alkali fusion to violanthrone; the reaction itself is complex, and the formation of by-products is unavoidable. However, it is an interesting fact that, although numerous modifications including stepwise syntheses have been suggested in the patent literature, the main technical process continues to be the alkali fusion of benzanthrone, and success in obtaining the dye with the desired shade in good yield depends essentially on the purity of the benzanthrone and the careful maintenance of optimum conditions of fusion. In the conversion of benzanthrone into dibenzanthrone by alcoholic potash fusion, isodibenzanthrone (see later) is also formed, but pure dibenzanthrone can be obtained by carrying out the fusion in naphthalene with the addition of an alkali salt of an organic acid, e.g. sodium acetate, and an oxidizing agent such as sodium nitrite.[68] It is considered that sodium acetate inhibits the decomposition of the 4,4′-dibenzanthronyl (IX) which is first produced and so prevents the formation of isodibenzanthrone, while

[67a] *Dyer* **100,** 706 (1948).
[68] du Pont, BP 430,665.

the oxidizing agent converts (IX) into dibenzanthrone. Other patents claim improvements when finely divided metals are added to the potash melt,[69] or by the addition of oxidizing agents before pouring the fusion product into water.[70] Among the various additions to potassium hydroxide and sodium acetate in the violanthrone melt which have been suggested may be mentioned an alkali phenoxide, an oxidizing agent (sodium nitrite) and sufficient alkali oxide (sodium oxide) to combine with the water present.[71] In the IG process,[2] benzanthrone (240 kg.) and "anthracene residues poor in carbazole" or naphthalene as flux are melted together at 120°, and a mixture (600 kg.) of 67–68% caustic potash and 27–28% caustic soda, which is the same composition as for Indanthrene Blue, together with anhydrous sodium acetate (50 kg.), is added. The reaction begins at 180°, and the melt is kept at 225–230° for 1–1.5 hours. The dye is purified by vatting, clarifying the solution with kieselguhr, filtering, and reoxidizing (yield 78.7%). Indanthrene Dark Blue BO is a mixture of violanthrone (91%), Indanthrene Black BGA (nitrated violanthrone) and Indanthrene Orange RRT (3%). A mixture of Indanthrene Dark Blue BO (51%), Navy Blue BF (30%) and Olive Green B (19%) is sold as Indanthrene Dark Blue GB.[3] Caledon Dark Blue 2R and BM are ICI brands of violanthrone with suitable additions for shading purposes.

A method of purifying crude violanthrone (as well as isoviolanthrone) is to stir at 50° or below with 94.5–97.5% sulfuric acid until the dye is converted into large crystals, dilute to about 90%, and filter the suspension.[72] Violanthrone of increased purity can be obtained by proceeding through (VIII) or (IX), but neither method is economical in comparison with the older direct fusion method. When benzanthrone is treated with manganese dioxide and concentrated sulfuric acid at 0° for several hours, (VIII) (dark yellow needles, m.p. 412–414°) is formed in about 50% yield, together with 2-hydroxybenzanthrone.[57, 73] In the manganese dioxide-sulfuric acid oxidation of benzanthrone to (VIII), and of (IX) and dibenzanthrone to 16,17-dihydroxydibenzanthrone (see later), products of greater purity are obtained by reducing the concentration of the acid to 82–85%.[74] The 4,4′-compound (IX) (yellow needles, m.p. 320–21°) is obtained when benzanthrone is heated with alcoholic potassium hydroxide.[57, 73] Both the dibenzanthronyls can be converted into pure dibenzanthrone in good yield: (VIII) by methanolic caustic potash fusion at 115–120° and (IX) by caustic potash fusion at 250°.[57, 73, 74a] The cyclization of (IX) and its substitution products, such as the dibromo and the dianthraquinonylamino compounds, may be effected by means of 80–90% sulfuric acid at 115–140° in presence of oxidizing agents like sodium nitrite and arsenate.[75] Titanium and zirconium tetrachlorides can be used for cyclizing (VIII) to dibenzanthrone.[76]

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[69] Kyrides and National Aniline, USP 1,908,712.

[70] Selden Co., USP 1,941,771.

[71] Waldron, Ulich and du Pont, USP 2,293,783.

[72] Perkins and du Pont, USP 2,180,299.

[73] See also IG, DRP 407,838; 409,689; 411,013; 431,774; 438,467; 450,999; Thomson, Thomas, and Scottish Dyes, BP 251,313. Weiss, *Trans. Faraday Soc.* **42**, 116 (1946), cites this oxidation as an example of a single electron transfer process in systems with conjugated double bonds possessing loosely bound π-electrons.

[74] du Pont, BP 430,914; ICI, BP 418,202; 405,706; see also Lee, Howell, and du Pont, USP 2,413,507.

The dye obtained by chlorination of violanthrone in nitrobenzene was marketed as Indanthrene Violet RT (CI 1100).[76a] Tetrachloroviolanthrone (Indanthrene Navy or Marine Blue RB), prepared by chlorination in trichlorobenzene or phthalic anhydride at 145°, and monobromoviolanthrone (Indanthrene Navy Blue BF) have approximately the same fastness properties as violanthrone, and halogenation is used for modifying the shade. It is important to carry out the chlorination in an organic solvent, since chlorination in an inorganic medium such as sulfuric acid leads to a dye different in the orientation of the chlorine atoms and inferior in the wet fastness of the shades.[6] Chlorosulfonic acid may be used as a solvent for bromination which can then be carried out using hydrobromic acid,[77] and the method has been applied to other types of anthraquinone vat dyes.[78] Dibenzanthrone and isodibenzanthrone halogenated in chlorosulfonic acid in presence of sulfur yield blue dyestuffs containing both halogen and sulfur, which are stated to be satisfactory both in fastness and dyeing properties.[79] 16,17-Diethyldibenzanthrone and the corresponding iso derivative may be prepared in the usual way from 2-ethylbenzanthrone; the former is blue, the latter blue-violet. The halogen derivatives dye in blue, gray, and brown-violet shades, and all are characterized by fastness to water-spotting, which is poor for dibenzanthrones having no substituents in the 16,17-positions.[80]

Nitro- and aminoviolanthrone. Nitration of dibenzanthrone with nitric acid in acetic acid, nitrobenzene or chloroacetic acid (the last being used in the current IG process) at 20–35° gives a mixture of mono-

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[74a] Pandit (unpublished work) has found that the conversion of (VIII) to dibenzanthrone is facilitated by the presence of about a fifth of its weight of glucose.

[75] Howell and du Pont, USP 2,388,743.

[76] Lecher, Scalera, Forster, and American Cyanamid, USP 2,416,931.

[76a] According to Fox, *J. Soc. Dyers Colourists* **65,** 520 (1949), Alizanthrene Navy Blue R (ICI) is probably 16,17-dichloroviolanthrone.

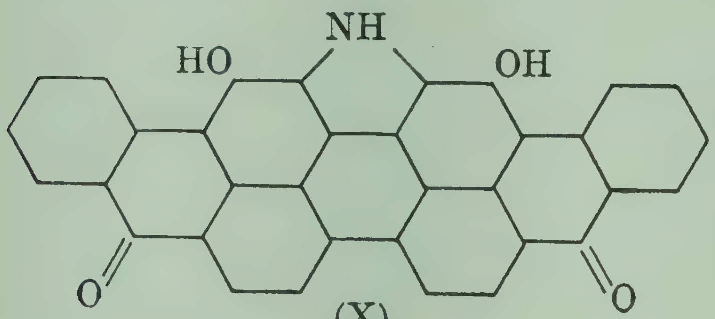
[77] IG, DRP Anm. J. 36,753.

[78] Ciba, SP 176,037; FP 724,482.

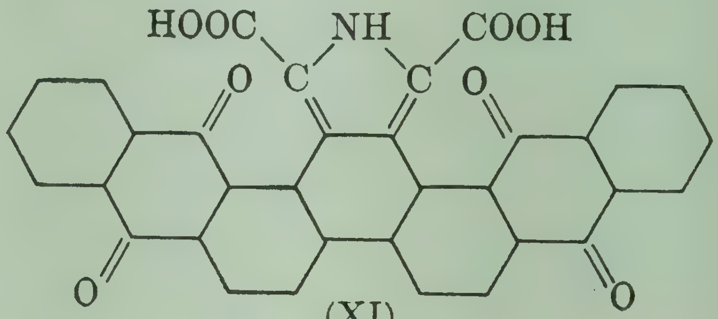
[79] IG, BP 419,666.

[80] Schlichting, Hrubesch and General Aniline and Film, USP 2,282,250.

and dinitrodibenzanthrone, dyeing an unlevel green (Indanthrene Green B) (Bally, 1904; CI 1102) of no practical value.[81] Since the nitro groups are reduced during vatting, the product on the fiber is a mixture of aminodibenzanthrones. When the green dye is oxidized on the fiber with hypochlorite (about 0.5% available chlorine) at room temperature, a deep fast black is produced.[82] Nitroviolanthrone is marketed under the name of Indanthrene Black B, BB, BGA and is an important and largely used dye. Other examples of commercial nitrodibenzanthrones are Caledon Black NB and 2BM, Ponsol Black BA, and Carbanthrene Black B. The position of the nitro groups and the constitution of the black dye produced on the fiber are still undetermined. Maki[83] considers that the nitro groups are in the 16,17-positions, since the corresponding diamino compound, on oxidation with chromic and sulfuric acid, gave first a brown alkali-soluble product (X) and ultimately a dicarboxylic acid (XI); the proposed structures, however, were based mainly on nitrogen estimation. On the assumption of the 16,17-orientation for the nitro groups, Maki concludes that the black dye, produced by hypochlorite oxidation of the diamine on the fiber, is the pyridazine derivative (XII). Bennett, Pritchard, and Simonsen[84] have obtained a carboxylic acid containing nitrogen by the chromic acid oxidation of dinitrodibenzanthrone, and this rules out the 16,17-orientation, since the oxidation of benzanthrone leads to anthraquinone-1-carboxylic acid. By analogy with other substitution reactions in the benzanthrone series, they regard dinitrodibenzanthrone as the 3,12-compound; oxidation gave a dinitrodianthraquinonyl dicarboxylic acid, which on reduction and deamination via the diazonium salt gave 2,2′-dianthraquinonyl-1,1′-dicarboxylic acid, identical with the product of the oxidation of dibenzanthrone itself. However, Pandit and Tilak[85] have synthesized authentic 3,12-diaminodibenzanthrone (XIII) by two routes, and found



(X)



(XI)

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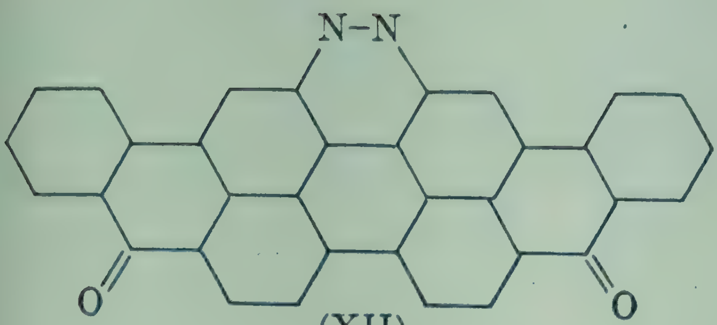
[81] BASF, DRP 402,641.

[82] BASF, DRP 185,222; 226,215; Ciba, DRP 448,908.

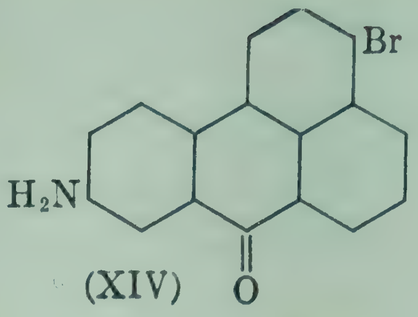
[83] Maki, Nagai, and Hayashi, *J. Soc. Chem. Ind. Japan,* Suppl. Binding **38,** 710B (1935).

[84] *JCS* 31 (**1943**).

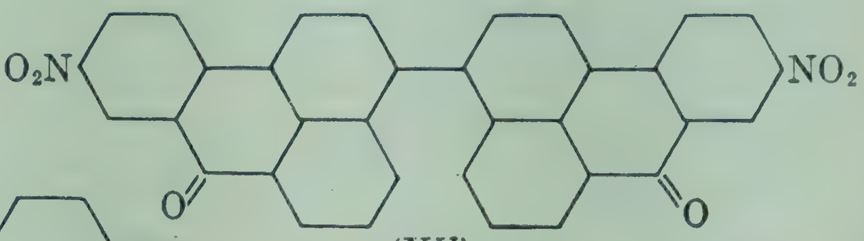
[85] Pandit, Tilak, and Venkataraman, *Proc. Indian Acad. Sci.* **32A,** 39 (1950).



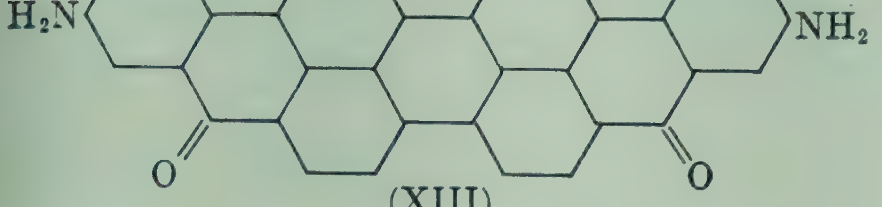
(XII)



(XIV)



(XV)



(XIII)

that it is different from the reduction product of dinitrodibenzanthrone. The syntheses of (XIII) were by the action of (a) palladized calcium carbonate, hydrazine, and methanolic caustic potash on 3-bromo-9-aminobenzanthrone (XIV), and (b) alcoholic caustic potash on 9,9′-dinitro-3,3′-dibenzanthronyl (XV). The constitution of (XV) follows from its oxidation to the known 6-nitroanthraquinone-1-carboxylic acid.

Dibenzanthrone may be aminated directly by the action of hydroxylamine, its *N*- or *O*-sulfonic acids, or their salts. The reaction is carried out in sulfuric acid (94–100%) solution in presence of vanadium or molybdenum compounds.[86]

Black dyes are now available in the benzanthrone series which do not involve dyeing a green shade and then oxidizing it on the fiber. These "Direct Blacks" can be prepared by several methods. There are three Indanthrene Direct Blacks in the current IG range—B, R and RB. The process for Indanthrene Direct Black RB is the condensation of tetrabromopyranthrone with α-aminoanthraquinone (0.5 mole) and aminodibenzanthrone (3.5 mole) in nitrobenzene solution in presence of copper oxide and sodium acetate.[2] Aminoviolanthrone is prepared in substance for this purpose by reduction of the nitro compound by means of sodium sulfide. From a dark blue vat Indanthrene Direct Black RB dyes rich black shades with excellent all-round fastness. It has been mentioned earlier in connection with the polyanthrimides and the carbazoles that the multiplication of anthraquinone residues has a marked effect on the fastness to alkali boil. Indanthrene Direct Black RB and similar dyes containing several anthraquinone nuclei exhibit excellent fastness to kier boiling, and such polyanthraquinonoid dyes also have the valuable properties of good affinity for cellulose and level-dyeing character.

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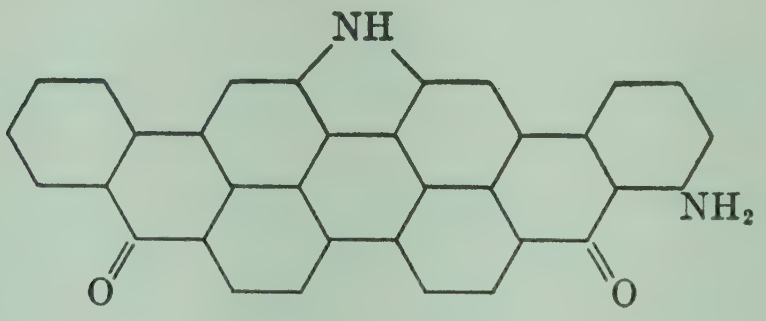
[86] Robson and ICI, BP 585,560; cf. Turski, DRP 287,756; BP 564,610; 626,661; BASF, BP 204,241. According to Ref. 76a, Indanthrene Gray 3B is 16,17-diaminodibenzanthrone.

Other Direct Blacks are made by modifications of the dibenzanthrone molecule in which products of undetermined structure are obtained by oxidation with chromic acid (e.g. Paradone Direct Black, probably a hydroxylated diquinone); or by the action of heat on nitrodibenzanthrone (Caledon Direct Black AC); or by reducing nitrodibenzanthrone, nitrodibenzanthronyl or nitroisodibenzanthrone in alcoholic suspension with sodium sulfide, and heating the amine without isolation at 210–215° with potassium hydroxide;[87] or by fusing diaminodibenzanthrone at 290° with caustic alkali, potassium chlorate and sodium phenoxide.[88] Nitrodibenzanthrones suitable for conversion into direct blacks can be prepared by nitration of dibenzanthrone in sulfuric acid. 3,3′-Dibenzanthronyl (VIII) is converted into gray to black dyes by nitration, reduction and heating with alcoholic potassium hydroxide so that nitrogen is not eliminated.[89] In the fusion of diamino-4,4′-dibenzanthronyl with alkalis, the use of alcoholic potash at 190–250° gives gray to black vat dyes fast to water-spotting.[90] Thus the dinitration of 4,4′-dibenzanthronyl, reduction of the nitro compound to the diamine and cyclization with alcoholic potassium hydroxide gives Indanthrene Grey 3G.[2] Dyes of this type can be prepared by the action of hydroxylamine on dibenzanthrone. If dibromodibenzanthrone, obtained by brominating dibenzanthrone in chlorosulfonic acid in presence of a halogen carrier, is condensed with two moles of α-aminoanthraquinone and then fused with either caustic alkali or aluminum chloride, the product gives fast gray to black shades from the vat.[91] The condensation product of a monoaminopyranthrone (2 moles) with dibromoviolanthrone (1 mole) dyes cotton in olive to greenish black shades from a red-violet vat.[92] The product of



Indanthrene Grey 3G

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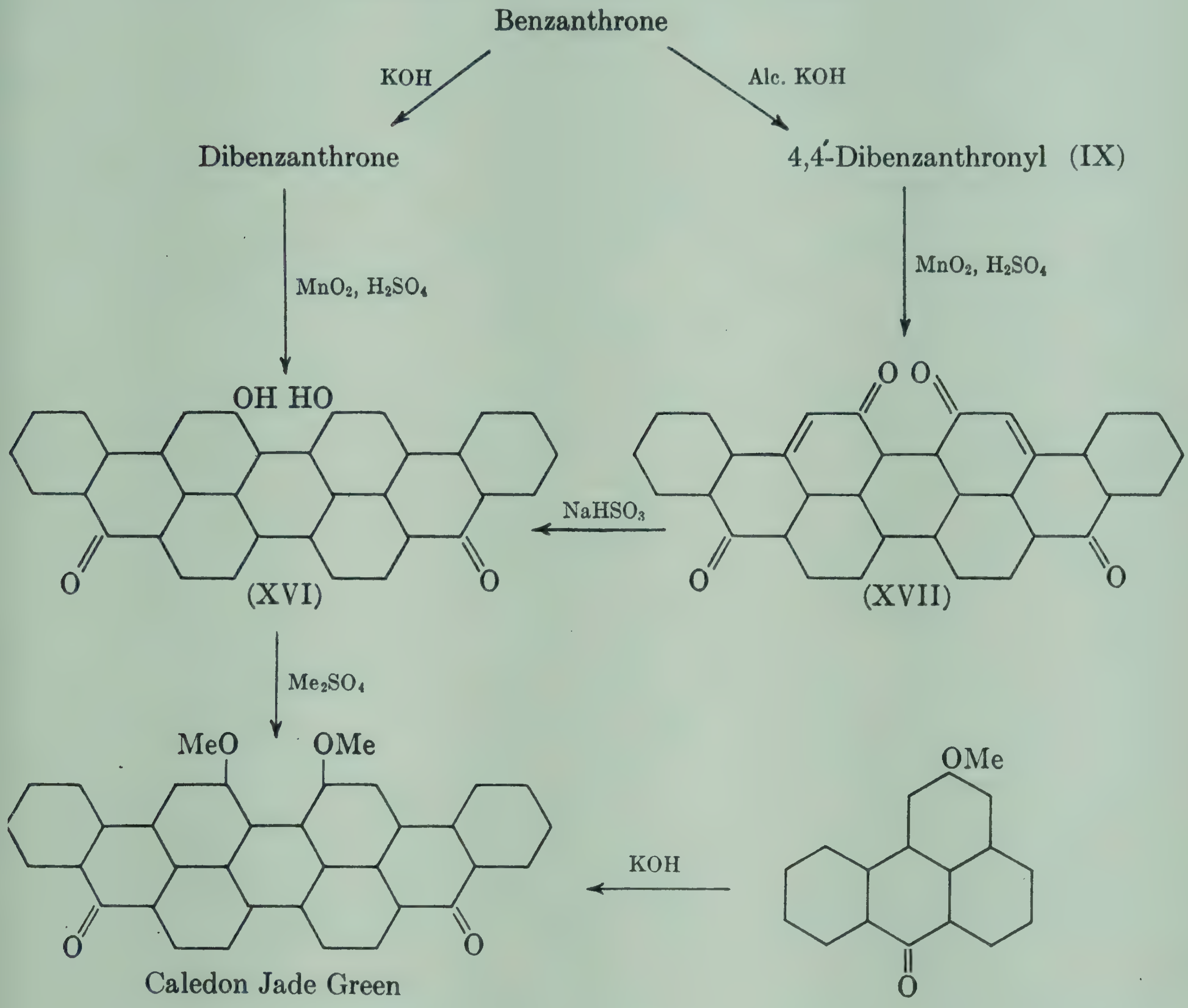
[87] Howell and du Pont, USP 2,310,087.
[88] Wuertz, Perkins, Granger, and du Pont, USP 2,334,891.
[89] Newport Co., BP 365,532.
[90] IG, BP 512,189.
[91] Fleysher and National Aniline, USP 2,232,700.
[92] Ogilvie and Allied Chemical and Dyestuff, USP 2,300,832.

the condensation of aminodibenzanthrone with 2,4-dinitrochlorobenzene dyes blue-gray shades fast to chlorine.[92a]

Dihydroxy- and dimethoxyviolanthrone. One of the major discoveries of the British dyestuff industry is Caledon Jade Green X (Indanthrene Brilliant Green B; FFB) (Davies, Fraser-Thomson and Thomas, 1920; CI 1101).[93] Oxidation of dibenzanthrone with manganese dioxide and sulfuric acid gives 16,17-dihydroxydibenzanthrone (XVI) which dyes

CHART 3
Syntheses of Caledon Jade Green


Benzanthrone
KOH
Alc. KOH
Dibenzanthrone
4,4′-Dibenzanthronyl (IX)
MnO₂, H₂SO₄
MnO₂, H₂SO₄
OH HO
O O
O
O
(XVI)
NaHSO₃
O
O
(XVII)
Me₂SO₄
MeO
OMe
O
O
Caledon Jade Green
KOH
OMe
O

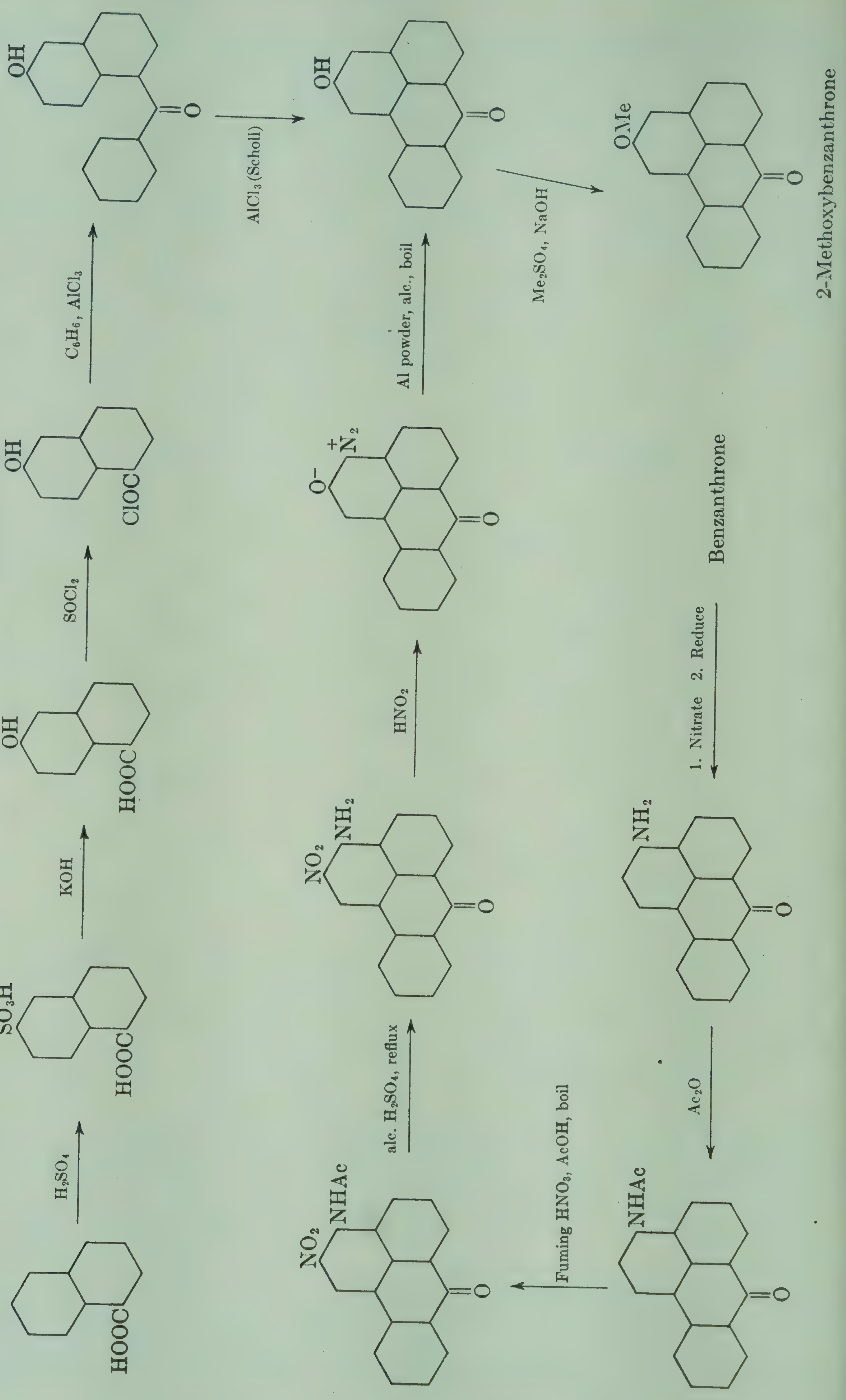
green shades with poor leveling properties; but methylation in nitrobenzene solution with dimethyl sulfate in presence of anhydrous potassium carbonate yields the dimethyl ether which dyes level shades of a bright and attractive bluish green with excellent fastness (light 7–8;

[92a] General Aniline and Film, USP 2,481,449.

[93] Davies, Thomson, Thomas and Scottish Dyes, BP 181,304; 193,431; see also Thomson, *J. Soc. Dyers Colourists* **42,** 124 (1926); *J. Soc. Chem. Ind.* **52,** 946 (1933); Howell and du Pont, USP 2,140,455.

CHART 4

SYNTHESIS OF 2-METHOXYBENZANTHRONE


HOOC
H_2SO_4
SO_3H
HOOC
KOH
OH
HOOC
$SOCl_2$
OH
ClOC
C_6H_6, $AlCl_3$
OH
O
$AlCl_3$ (Scholl)
OH
O
NO_2
NHAc
O
alc. H_2SO_4, reflux
NO_2
NH_2
O
HNO_2
O^-
$\overset{+}{N}_2$
O
Al powder, alc., boil
Me_2SO_4, NaOH
OMe
O
2-Methoxybenzanthrone
Fuming HNO_3, AcOH, boil
NHAc
O
Ac_2O
NH_2
O
1. Nitrate 2. Reduce
Benzanthrone

alkali boil and chlorine 4–5).[93a] The constitution of the dye has been confirmed by its synthesis from 2-methoxybenzanthrone (brownish yellow crystals, m.p. 174–174.5°), which can be prepared by several methods (Chart 4).[94]

The IG method (Lüttringhaus and Neresheimer, 1922)[95] for the preparation of 16,17-dimethoxydibenzanthrone proceeds through 4,4′-dibenzanthronyl (IX), prepared by heating benzanthrone (200 kg.) with potassium hydroxide (500; 90%) and anhydrous sodium acetate (60) in isobutyl alcohol (385) at 112° for 1–4 hours, and diluting with water (1000). Two layers are formed, and the upper layer is separated and oxidized at 50° with 12% sodium hypochlorite (80) in water (600). After removal of isobutyl alcohol by steam distillation, (IX) is collected and dried (yield 82%). On dissolving (IX) (150 kg.) in 96% sulfuric acid (4000) and water (560), and oxidizing with manganese dioxide (192) at 25–30° for 4 hours, pouring into aqueous sodium bisulfite and boiling, 16,17-dihydroxydibenzanthrone (XVI) is obtained in nearly quantitative yield. The direct oxidation product is 16,17-diketodibenzanthrone (XVII) which is then reduced to (XVI) by the action of bisulfite. Methylation is effected by heating (XVI) (150 kg.) in trichlorobenzene (2370) with methyl *p*-toluenesulfonate (245) and anhydrous potassium carbonate (180) at 210° for 4 hours. After cooling to 150° and distilling down to dryness *in vacuo*, the product is marketed as Indanthrene Brilliant Green B. A purer brand, Indanthrene Brilliant Green FFB, is made by filtering the hot trichlorobenzene solution at 150° in a pressure filter, washing the product with hot trichlorobenzene and drying (yield 144 kg.). In both cases, the dyestuff is finally dispersed from sulfuric acid.[2] Methylation of (XVI) by dimethyl sulfate and sodium carbonate in boiling trichlorobenzene in presence of phenol gives an "improved green vat dye" by reducing any (XVII) formed during the reaction.[95a]

Partially alkylated products may be separated from dialkoxydibenzanthrones by treatment with aqueous alkali and pyridine in which the former dissolve.[96]

Halogenation of dimethoxydibenzanthrone must be carried out under conditions which do not result in demethylation by the hydrogen halide formed in the reaction. Bromination can be conveniently carried out in a mixture of 96% sulfuric acid and 24% oleum at 40°; after the addition of bromine, about a sixth of its weight of sodium nitrite is added. The dibromo compound is Caledon Jade Green G or 2G (Indanthrene Brilliant Green GG), and the 4G brand is a mixture of Green 2G and Algol Yellow 8G (Indanthrene Yellow GF).[97]

[93a] According to Ref. 76*a*, Caledon Jade Green 3BS is probably diethoxydibenzanthrone.

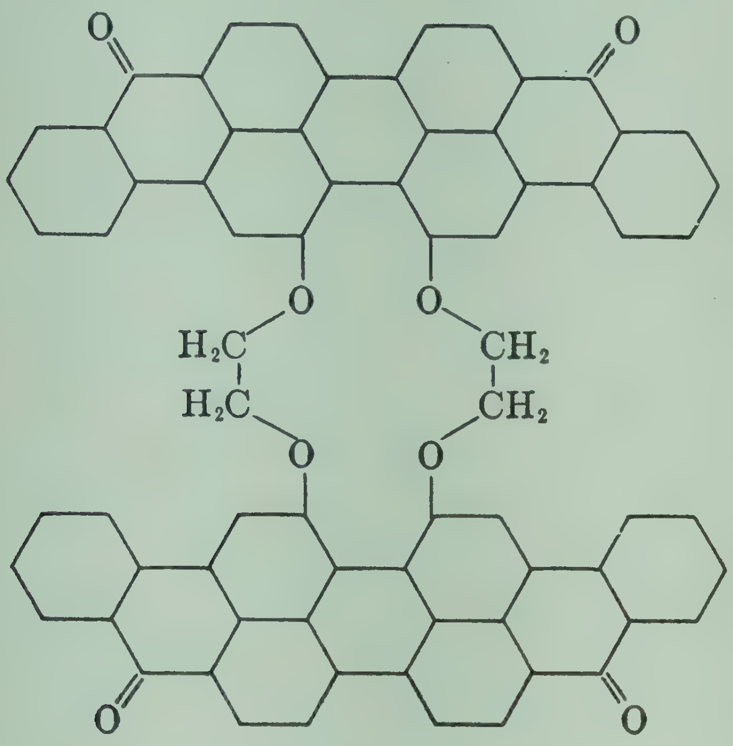
[94] Schirmacher, Zahn, Ochwat, and Wilke, USP 1,614,398; DRP 413,738; see also Baddar, *JCS* 1088 (**1948**).

[95] BASF, DRP 411,013.

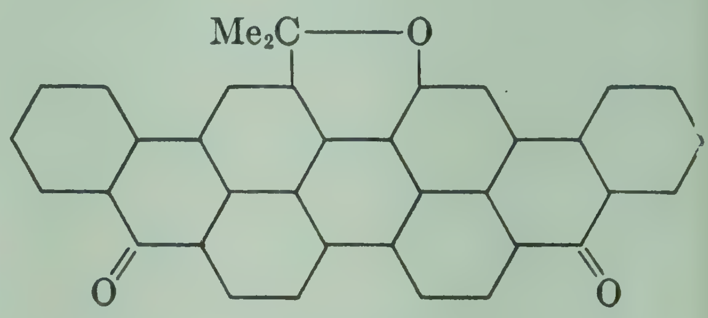
[95a] Cincinnati Chemical Works and Ciba, BP 636,008.

[96] Beckett and ICI, USP 2,388,665; BP 581,259.

The ethylene ether of (XVI) is a greenish blue dye (Caledon Dark Blue G). The IG analog, Indanthrene Navy Blue G, is prepared by alkylating dihydroxydibenzanthrone with ethylene dibromide or β-chloroethyl *p*-toluenesulfonate.[2, 98] In its fastness properties it is similar to Indanthrene Dark Blue BO, which is much redder in tone.



Indanthrene Navy Blue G



(XVIII)

16,17-Dihydroxydibenzanthrone (XVI) has been alkylated with β,β'-dihydroxydiethyl ether and similar reagents to obtain dyestuffs greener in shade than the corresponding dimethoxy derivative.[99] The alkylation of dihydroxydibenzanthrone in some cases is best carried out by using one of its dry alkali-metal salts as starting material.[100] Bishydroxyalkyl ethers of (XVI), prepared by heating it with an aliphatic or cycloaliphatic α,β-epoxide and a heterocyclic base are blue-green vat dyes, and they can be sulfated to form acid wool dyes of similar shades.[101]

Mono*iso*propyl or *iso*butyl ethers of (XVI) are converted by heating above 150° in a solvent under alkaline conditions into bluish-green vat dyes fast to acid and alkali; they differ from the normal ethers of (XVI) in their resistance to acid hydrolysis. They may be sulfonated to yield green acid wool dyes without loss of alkyl groups. It is suggested[102] that loss of water has taken place between the 16-hydroxyl and a hydrogen atom of the secondary alkyl group forming a pyran ring as in (XVIII). 16,17-Dihydroxydibenzanthrone (XVI) gives a stable leuco compound,[103] which can be isolated as the monosodium salt from a hydrosulfite vat by reducing the pH to 9–12 at 60–90° until precipitation is complete; this compound dissolves in sulfuric acid with a blue color and is unchanged on precipitation, even after heating at 100°. Derivatives of this and of the normal leuco compound have been described; the former also esterifies normally to the disulfuric ester.[104] A dinitro derivative of (XVI) can be prepared and reduced to the mono- or diamine.[105] 15-Amino- or 15,18-diamino-16,17-dihydroxydibenzanthrone is converted into 15,16,17-tri- or 15,16,17,18-tetrahydroxydibenzanthrones respectively by the action of water or dilute acids or bases,[106] and these may be alkylated to yield blue, green, and greenish-blue vat dyes.[107] A simpler method for the preparation of 15,16,17-trihydroxydibenzanthrone consists in heating 16,17-diketodibenzanthrone (XVII) in sulfuric acid alone or with a catalyst and then reducing the resultant 15-hydroxy-16,17-diketodibenzanthrone.[108] Blue, green, or gray vat dyes are obtained when amino- or diaminodihydroxydibenzanthrones, in which at least one NH_2 is *ortho* to a hydroxyl group, are converted into oxazoles.[109] 1,14,16,17-Tetramethoxydibenzanthrone is a gray-green vat dye.[110] Dibenzanthrone and its derivatives in general are violet, blue, green or black dyes, but red vat dyes of undetermined structure have also been described. They are prepared by interaction of (XVI) with aromatic carboxyl halides in presence of ferrous or ferric chloride, and treating the resulting bluish dyes with ammonia, amines, acid amides, or phenylhydrazine.[111]

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[97] Fierz-David, Künstliche Organische Farbstoffe, Springer, Berlin, 1926; IG, DRP 436,828.

[98] See also Stallmann and du Pont, BP 546,997; Maki, *J. Soc. Chem. Ind. Japan* **46,** 1256 (1943).

[99] du Pont, USP 1,947,047.

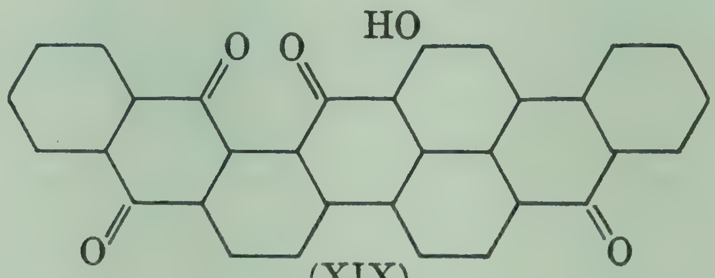
[100] Stallmann and du Pont, USP 1,950,366.

[101] Young, Gey, and du Pont, USP 2,302,733. See also USP 2,183,626–7.

Fluorescent dyes for coloring petroleum oils are made by treating hydroxydibenzanthrones or isodibenzanthrones, or their leuco derivatives, in an anhydrous organic solvent with chlorocarbonic esters such as ethyl and octadecyl; an example is the bis-carbethoxy derivative of leucodimethoxydibenzanthrone.[112]

[102] du Pont, BP 434,152.
[103] du Pont, USP 2,183,625.
[104] du Pont, USP 2,188,320.
[105] IG, BP 442,860.
[106] IG, DRP Anm. J. 52,762.
[107] IG, BP 462,659.
[108] IG, DRP Anm. J. 52,858.
[109] IG, BP 456,579.
[110] Maki and Kikuchi, *Ber.* **71**, 2031 (1938).
[111] IG, BP 480,284; 504,478.
[112] du Pont, USP 2,258,400.

The relationship between the dibenzanthrones and the dibenzopyrenequinones is indicated by the fact[2, 113] that oxidation of 16,17-diketo- or dihydroxy-dibenzanthrone by means of nitric and sulfuric acids in presence of vanadium pentoxide yields 9-hydroxy-1,2-benzo-6,7-(2′,1′)-anthraquinonopyrene-3,8-quinone (XIX). Methylation gives a fast yellow dye, and orange vat dyes of similar type have also been described, but they are too expensive for commercial development.



(XIX)

It has been suggested that vat dyes such as Caledon Jade Green can be used for standardizing coal assay apparatus, since they can be obtained pure in large quantities.[114] Making carbonization assays of a number of vat dyes, it has been found that diethoxydibenzanthrone gives a larger gas volume and calorific value than the dimethoxy compound, the results indicating the presence in bituminous coals of aliphatic peripheral groups.

Isodibenzanthrone (see Chart 5) (Bally and Wolff, 1906; CI 1103) was first made by heating 3-chlorobenzanthrone (I) with alcoholic caustic potash at 150°;[115] (I) is readily obtained by chlorination of benzanthrone in aqueous suspension at 100°. The mode of formation of isoviolanthrone from benzanthrone is probably by 3-chlorobenzanthrone yielding the anion (II) which replaces chlorine in another molecule of 3-chlorobenzanthrone giving (III); repetition of the processes of proton liberation and halogen replacement then leads to isoviolanthrone.[116]

The modern method of manufacture is a great advance on the original process, and proceeds through 3,3′-dibenzanthronyl sulfide or selenide.[117] The corresponding sulfone may also be used, and the temperature of the water-bath is then adequate for the conversion. 3,3′-Dibenzanthronyl sulfide is converted into isoviolanthrone in 80% yield by refluxing for 2 hours with potassium hydroxide (1.5 parts) in isobutanol. Perkins describes a very short process in which 3-bromobenzanthrone is converted into the dibenzanthronyl selenide or sulfide by heating with an alkali

[113] IG, BP 480,882.

[114] Gibson *et al.*, *Inst. Fuel Wartime Bull.* Feb. 128 (1945).

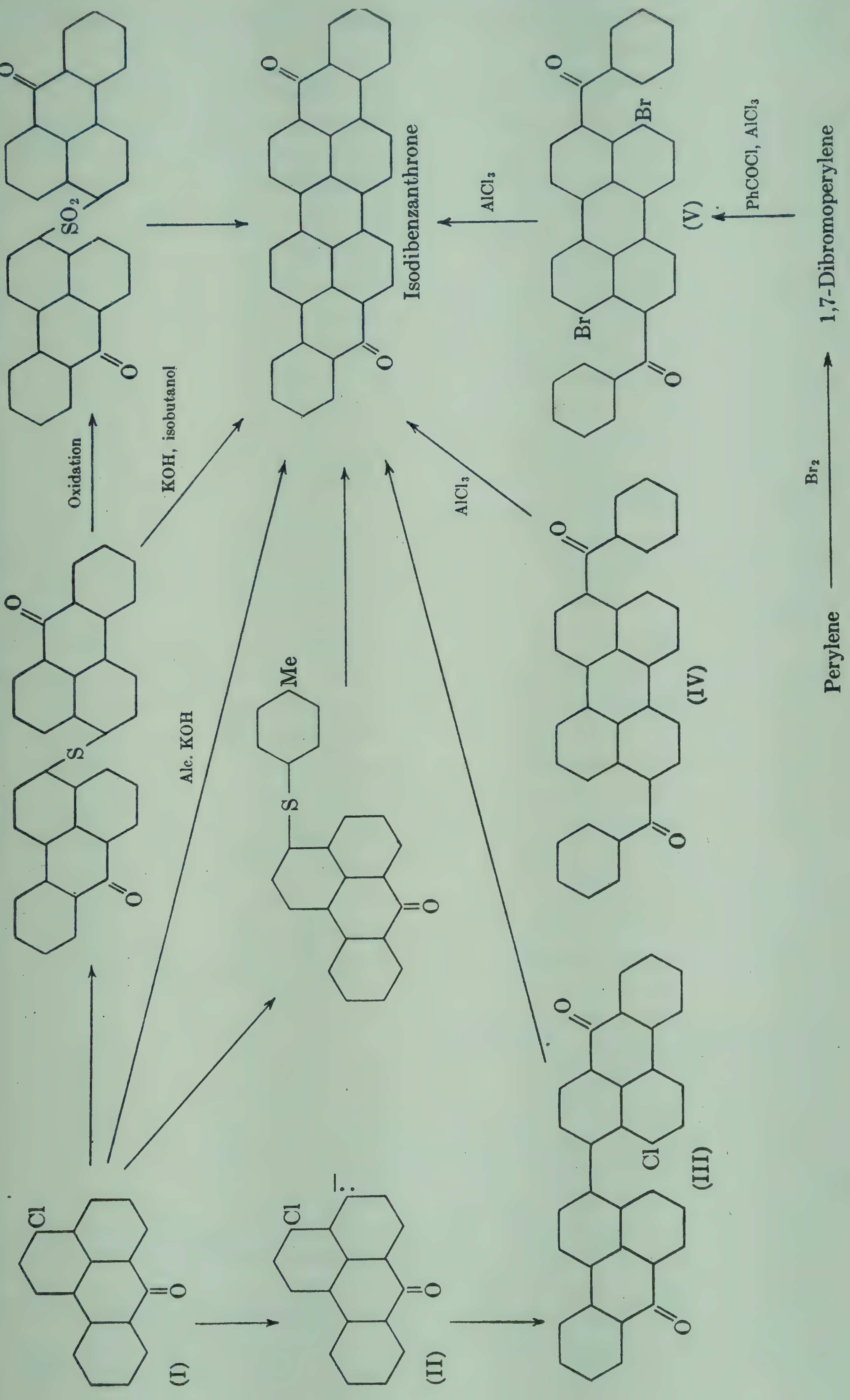
[115] BASF, DRP 194,252.

[116] Bradley and Jadhav, *JCS* 1622 (**1948**); contrast Schwenk, *Chem. Ztg.* **52,** 62 (1928).

[117] du Pont, BP 370,905; IG, DRP 441,748; 443,022; 448,262; ICI, BP 367,462. See also Nagai, *J. Soc. Chem. Ind. Japan* **45,** Suppl. binding, 149, 151 (1942).

CHART 5

SYNTHESES OF ISODIBENZANTHRONE


Cl
(I)
Cl
(II)
Cl
(III)
S
O
O
Oxidation
SO₂
O
O
KOH, isobutanol
Alc. KOH
S
Me
O
Isodibenzanthrone
O
O
AlCl₃
AlCl₃
O
O
(IV)
Br
Br
O
O
(V)
PhCOCl, AlCl₃
Perylene
Br₂
1,7-Dibromoperylene

metal selenide or sulfide; caustic potash is added, and isodibenzanthrone is formed on heating.[118]

3,3′-Dibenzanthronyl selenides are obtained by treating (I) or its derivatives with alkali selenides in water or alcohol. The diselenide or the hydrogen selenide may also be obtained according to the conditions.[119] The diselenide and the sodium selenide may be converted into the dibenzanthronyl selenide by heating with a solvent with or without a metal such as copper.[120] Alternatively, the dibenzanthronyl selenide may be obtained from the sodium benzanthronyl selenide and 3-halogenobenzanthrone.[121] 3,3′-Dibenzanthronyl selenide on fusion with sodium alkoxide yields isodibenzanthrone of high purity.[122] A halogeno-3,3′-dibenzanthronyl selenide may be condensed with an aminoanthraquinone and the resulting imide may be fused with potash to give vat dyes.[123] A mixed type, anthraquinonyl 3-benzanthronyl selenide, is obtained by condensing a halogenoanthraquinone with a 3-benzanthronyl sodium selenide. Some of these products are violet to blue vat dyes.[124] 3-Chloro-3′,4-dibenzanthronyl is formed in 25% yield by treating (I) with alcoholic potash at 100° for an hour, and yields isodibenzanthrone on further fusion.[125]

The constitution of isodibenzanthrone has been confirmed by its formation from 3,9-dibenzoylperylene (IV) on baking with aluminum chloride; cyclization of 3,9-dibromo-4,10-dibenzoylperylene (V) proceeds more readily.[126] Oxidation of isodibenzanthrone with chromic and acetic acids gives 1,2,5,6- or *trans*-bis-angular diphthaloylanthraquinone.[126a]

An interesting method for the preparation of 3,4′-dibenzanthronyl (VI) is by the condensation of methyleneanthrone (VII) with 4-benzanthronylacrylic acid (VIII) in nitrobenzene which acts both as solvent and oxidizing agent.[127]

Isodibenzanthrone (Isoviolanthrone; Indanthrene Violet R) has been superseded by its halogenated derivatives which are brighter and faster,

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[118] Perkins and du Pont, USP 2,153,312.

[119] du Pont, USP 1,965,855.

[120] du Pont, USP 1,999,996.

[121] du Pont, USP 1,999,999.

[122] Scalera, Forster and American Cyanamid, USP 2,468,606.

[123] du Pont, USP 1,977,242.

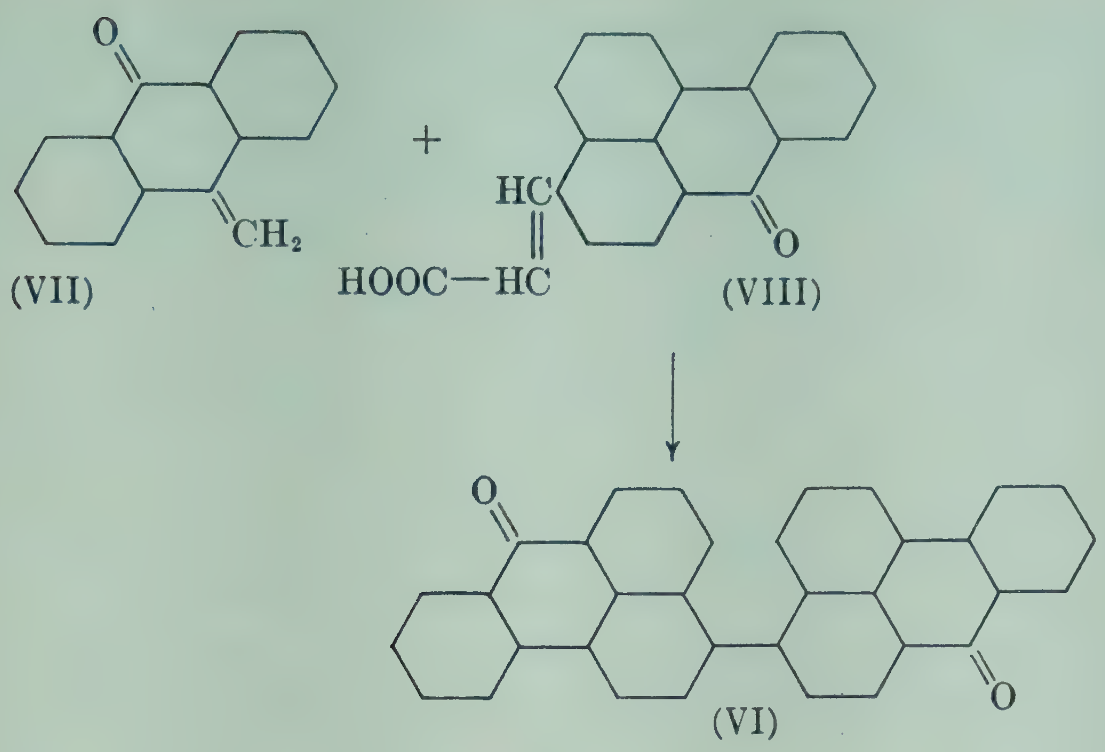
[124] du Pont, USP 1,999,997.

[125] Nakanishi, *J. Chem. Soc. Japan* **55**, 483 (1934).

[126] Scholl and Seer, *Ann.* **394**, 126 (1912); Zinke *et al. Ber.* **58**, 323, 799, 2222 (1925); Marschalk, *Bull. soc. chim.* **41**, 706 (1927).

[126a] Scholl and Meyer, *Ber.* **61**, 2550 (1928). See also Maki and Nagai, *Ber.* **70**, 1867 (1937).

[127] du Pont, USP 2,136,998.



and have better leveling properties.[128] Chlorination, e.g., by means of sulfuryl chloride in nitrobenzene, gives a dichloro derivative (Indanthrene Brilliant Violet RR; Caledon Brilliant Purple 4R; CI 1104). Bromination in chlorosulfonic acid in presence of a little sulfur gives Indanthrene Brilliant Violet 3B, which contains 15.5% bromine and 1.8% chlorine, and dyes a bluer shade.[3] Indanthrene Brilliant Violet 3B has also been stated to be 6,15-dibromoisoviolanthrone, having a bromine content of 26–26.5%, introduced by the action of bromine (75 kg.) and iodine (20) on isoviolanthrone (200) in chlorosulfonic acid (1600) at 50° for two hours.[4a] The theoretical bromine content of dibromoisoviolanthrone is 26.1%, and of monobromoisoviolanthrone 15.0%. These Brilliant Violets are superior to the early representatives (the dichloro compound, Indanthrene Violet RR; and the dibromo, Violet B extra; CI 1105) because of the much greater purity of the isodibenzanthrone now submitted to halogenation. The purple and violet dyes of the dibenzanthrone and isodibenzanthrone series have a tendency to redden on moistening, and the defect is remedied if the dyes are halogenated by special methods, e.g., by chlorination in a solvent at temperatures below 130° so as to form a dichloro derivative. Cibanone Blue RA and G, Cibanone Violet BW, and Alizanthrene Navy Blue are dyes of this type.[129]

4-Methylbenzanthrone is obtained together with other methylbenzanthrones when 2-methylanthraquinone is submitted to the benzanthrone reaction. When the isomers which are left after extracting 4-methylbenzanthrone are used for the production of isodibenzanthrones, the dyes are bluer in shade than isodibenzanthrone itself. The mixture of isomerides is brominated in 80–85% sulfuric acid and then fused with alkali directly or after conversion into the sulfide or selenide derivatives.[130]

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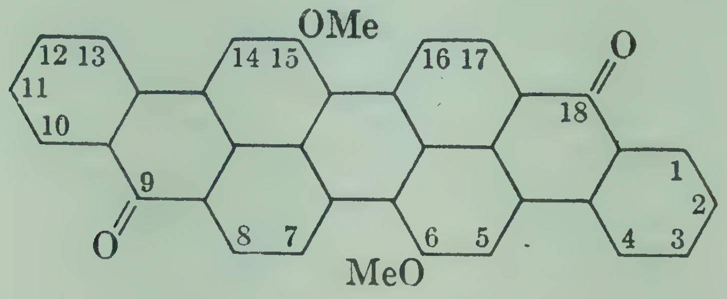
[128] BASF, DRP 217,570.

[129] Fraser-Thomson in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. I, Longmans, London, p. 402.

Caledon Ming Blue X is 6,15-dimethoxyisoviolanthrone.[130a] Greenish blue shades are obtained by the introduction of halogen; thus when



Caledon Ming Blue X

9,9′-dichloro-3,3′-dibenzanthronyl diselenide is fused with alcoholic potash, oxidized with manganese dioxide and sulfuric acid, the diquinone reduced with sodium bisulfite, and the dihydroxy compound is methylated, the product gives a greener shade than Caledon Ming Blue X.[131] A greenish blue dye is also obtained by halogenation of 6,15-dialkoxyisodibenzanthrones, prepared by alkylating the oxidation product of isodibenzanthrone.[132]

Oxidation of aminoisodibenzanthrones with sodium nitrite and dilute sulfuric acid at 40–45° for several hours, followed by a short treatment at the boil, gives gray to black dyes which are fast to light, washing and chlorine.[133]

Miscellaneous derivatives of benzanthrone. Cyananthrene O or Indanthrene Dark Blue BT (Bally and Isler, 1904; CI 1117), prepared by the alkali fusion of "benzanthronequinoline," is now obsolete. "Benzanthronequinoline," obtained by the action of glycerol and sulfuric acid on β-aminoanthraquinone, was formulated by Bally[134] as being probably a 5,6-pyridino derivative of benzanthrone. The angular, as against the linear orientation, was proved by the fact that "benzanthronequinoline" was obtained by the action of glycerol and sulfuric acid on 1,2(*N*)-pyridinoanthraquinone (5,6-phthaloylquinoline); Graebe had prepared this angular pyridinoanthraquinone earlier from Alizarin Blue by zinc dust distillation to pyridinoanthracene and subsequent oxidation.[134] Pandit and Tilak[85] have now found that Bally's benzanthronequinoline is the 9,8-derivative (I). 9-Aminobenzanthrone (II; red needles, m.p. 225–6°),

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[130] Ciba, BP 441,041.

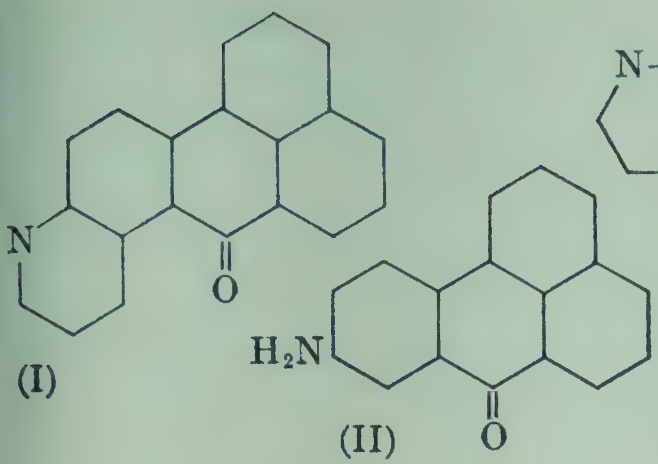
[130a] Geake, *Trans. Faraday Soc.* **37,** 68 (1941).

[131] du Pont, USP 2,170,381.

[132] IG, FP 810,512; see also DRP 442,511.

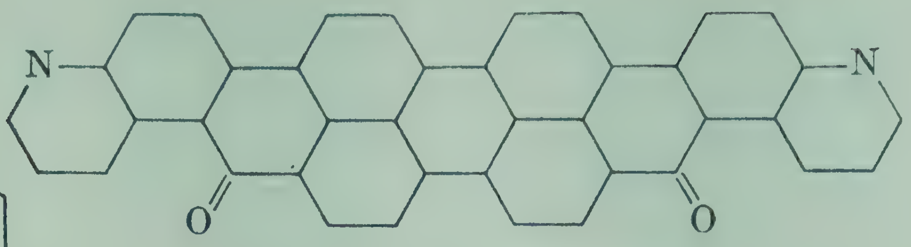
[133] Fleysher and Allied Chemical and Dyestuff, USP 2,400,195.

[134] *Ber.* **38,** 196 (1905); Bally and Scholl, *Ber.* **44,** 1656 (1911); Graebe, *Ann.* **201,** 333 (1880).



(I)

(II)



Indanthrene Dark Blue BT

prepared earlier by Copp and Simonsen[135] through a lengthy route, was synthesized by nitrating 3-bromobenzanthrone to 3-bromo-9-nitrobenzanthrone, which was reduced to 3-bromo-9-aminobenzanthrone (red needles, m.p. 274°) and dehalogenated by palladium, methanolic caustic potash and a few drops of hydrazine[136] to (II), together with 3,12-diaminodibenzanthrone. The Skraup reaction on (II) gave (I), identical with Bally's "benzanthronequinoline" (bright yellow needles, m.p. 251°). Consequently, Indanthrene Dark Blue BT has the indicated structure.[136a]

When β-aminoanthraquinone is treated with glycerol, sulfuric acid and arsenic pentoxide, 5,6-phthaloylquinoline and 6,7-phthaloylquinoline are formed. The former gives Bally's "benzanthronequinoline" by the action of glycerol, sulfuric acid, and copper bronze, and the fact that Bally and Scholl isolated 6,7-phthaloylquinoline, and not the isomeric angular compound, from the products of the action of glycerol and sulfuric acid on β-aminoanthraquinone indicates that the angular compound undergoes very facile conversion into (I). The Bally reaction is complex, and at least one other benzanthronequinoline can be isolated, and this compound is one of three benzanthronequinolines which are formed by the action of glycerol, sulfuric acid and copper on 6,7-phthaloylquinoline.[136b]

3-Bromobenzanthrone (III) can be prepared in nearly quantitative yield by bromination of benzanthrone; it is dispersed from sulfuric acid, and heated at 70–75° in aqueous chloroacetic acid suspension with hydrochloric acid and bromine, and finally with sodium hypochlorite; excess halogen is then destroyed by treatment with sodium bisulfite solution. Treatment of benzanthrone with the calculated quantity of bromine and an equivalent amount of sulfuryl chloride in nitrobenzene at 80–90° also gives pure (III) in 95% yield. While sulfuryl chloride chlorinates benzanthrone as usual, in the presence of bromine it acts as an oxidizing agent only, and (III) is formed in a very economical manner.[137] In the bromination of benzanthrone two moles of bromine are absorbed by two of benzanthrone, and a complex compound is then formed from one mole of the salt-like dibromo derivative and one of benzanthrone.[138]

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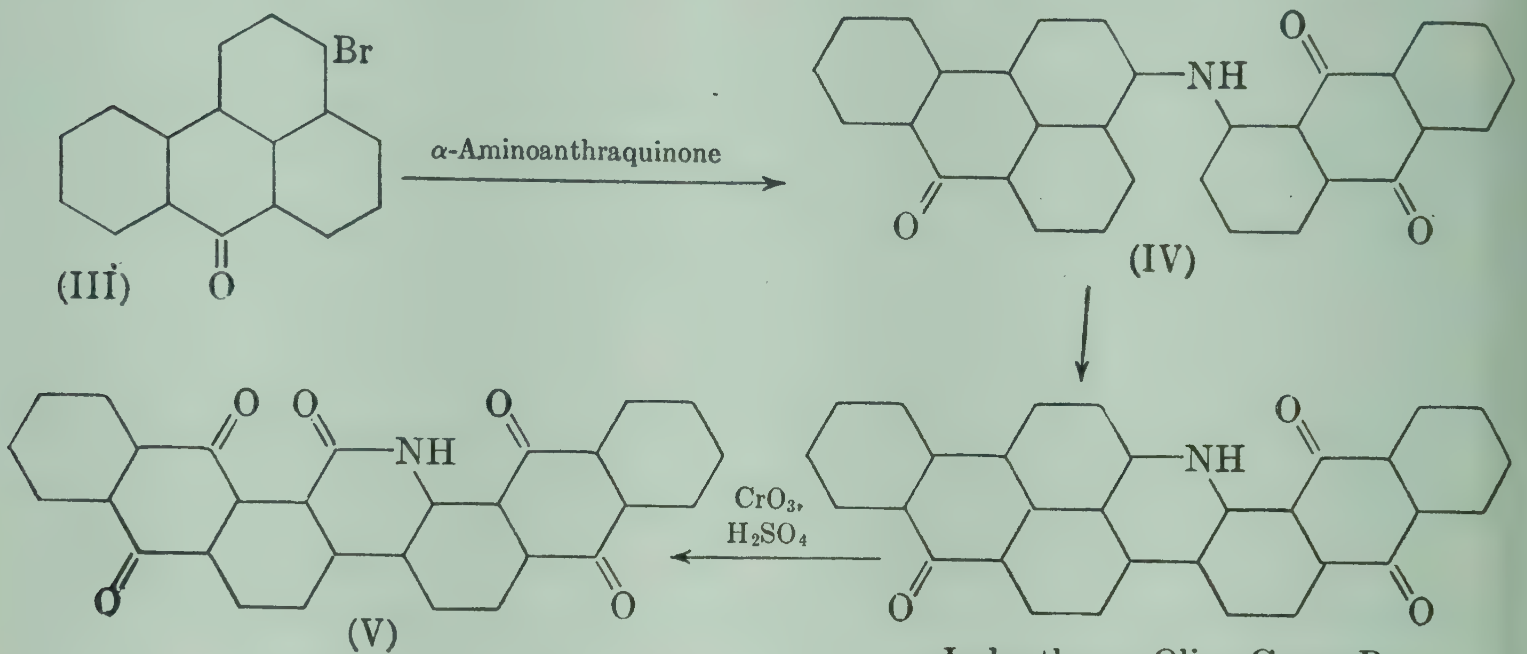
[135] *JCS* 209 (**1942**).

[136] Busch, Weber and Zink, *J. prakt. Chem.* **155,** 163 (1940).

[136a] Bradley (private communication) has shown that Indanthrene Dark Blue BT is the isoviolanthrone derived from (I).

[136b] Pandit, unpublished work.

When (III) is condensed with α-aminoanthraquinone in molten naphthalene in presence of copper oxide, and the secondary amine (IV) is treated with potassium hydroxide in boiling isobutyl alcohol for 3 hours, cyclization to an acridine takes place and the product is Indanthrene Olive Green B,[2, 139] a dye with light fastness 8, chlorine fastness 4–5, and soda-boil fastness 4. The substance exists in two modifications which differ in their solubility in pyridine.[140] Indanthrene Olive Green B and its derivatives can be purified by vatting and salting out the leuco compound.[140a] The constitution of Indanthrene Olive Green B is shown by its oxidation to a phenanthridone (V).[141] Oxidation of dibenzanthrone or of 4,4′-dibenzanthronyl by chromic acid yields 2,2′-dianthraquinonyl-1,1′-dicarboxylic acid which has also been synthesized from 2-bromo-1-cyanoanthraquinone. The dicarboxylic acid yields a half amide which undergoes the Hofmann reaction and then cyclizes by dehydration to (V).[142]



(III) (IV) (V) Indanthrene Olive Green B

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[137] Perkins, Deinet, and du Pont, USP 2,180,835.

[138] Müller and Wiesemann, *Ber.* **69B**, 2173 (1936).

[139] Maki and Kikuchi, *J. Soc. Chem. Ind. Japan* **42,** 316B (1939); BASF, DRP 212,471; IG, DRP 504,016; 507,344; 509,422. See also Hironaka and Tono, JP 172,744; Ciba, BP 613,836; General Aniline and Film, USP 2,392,794.

[140] Microfilm FDX 14.

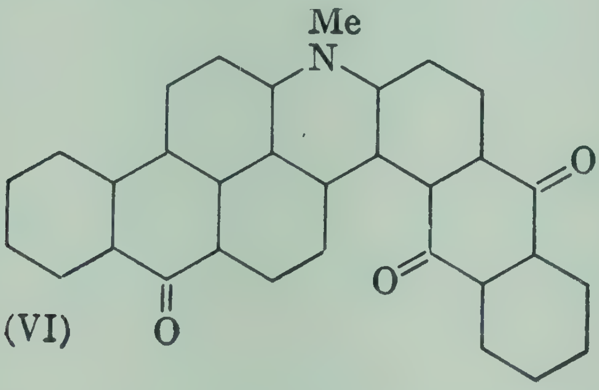
[140a] Scalera and American Cyanamid, USP 2,483,238.

[141] IG, DRP 499,352.

[142] Scholl, Müller, and Böttger, *Ber.* **68B,** 45 (1935).

If 1,5-diaminoanthraquinone is condensed with one mole of (III), and after cyclization the remaining amino group is benzoylated, the product is Indanthrene Olive GB (not mentioned in the I.G. shade card); and chlorination gives Olive Green GG.[139] Olive Green GG has excellent fastness properties (light 7–8; alkali boil and chlorine 4–5). By introducing suitably substituted amino groups in the 4-, 5- or 8-position of the anthraquinone residue, gray dyes are produced.[143] Mixtures of the Indanthrene Olive Green GB and GG type of dye with a dibenzanthrone or isodibenzanthrone dye black shades with excellent fastness to light, washing and kier boiling.[144] Vat dyes of deep shades are obtained by condensing one mole of (III) with an anthraquinonecarbazole containing two amino groups, cyclizing to an acridine, and acylating the remaining amino group.[145]

Dyes of the Indanthrene Olive Green type can be prepared by using 3-alkoxybenzanthrones in place of (and occasionally in preference to) the 3-halogeno compounds. Condensing 3-methoxybenzanthrone with β-aminoanthraquinone, cyclizing to the acridine, and then methylating, a gray vat dye (VI) is obtained.[145a]



(VI)

Dibromination of benzanthrone in chlorosulfonic acid and monohydrate at 20–45° for 15 hours, using iodine as catalyst, gives a 97% yield of the 3,9-dibromo compound (VII),[2] useful for the preparation of derivatives of Indanthrene Olive Green (Chart 6). Indanthrene Olive T (a dye with light fastness 7–8 and fastness to soda-boil and chlorine 4–5) has been assigned both the indicated anthrimide[2] and the corresponding carbazole structures.[4a] By treatment of Indanthrene Olive T with aluminum chloride and sulfuryl chloride, a novel shade of olive with high light fastness is obtained.[2] Fast gray vat dyes can be prepared from mixed chlorobenzanthrones (Cl 13.5%) by condensation with α-aminoanthraquinone and cyclization.[146] Bluish-gray dyes are obtained by

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[143] IG, BP 358,074; 362,432.

[144] IG, BP 468,037.

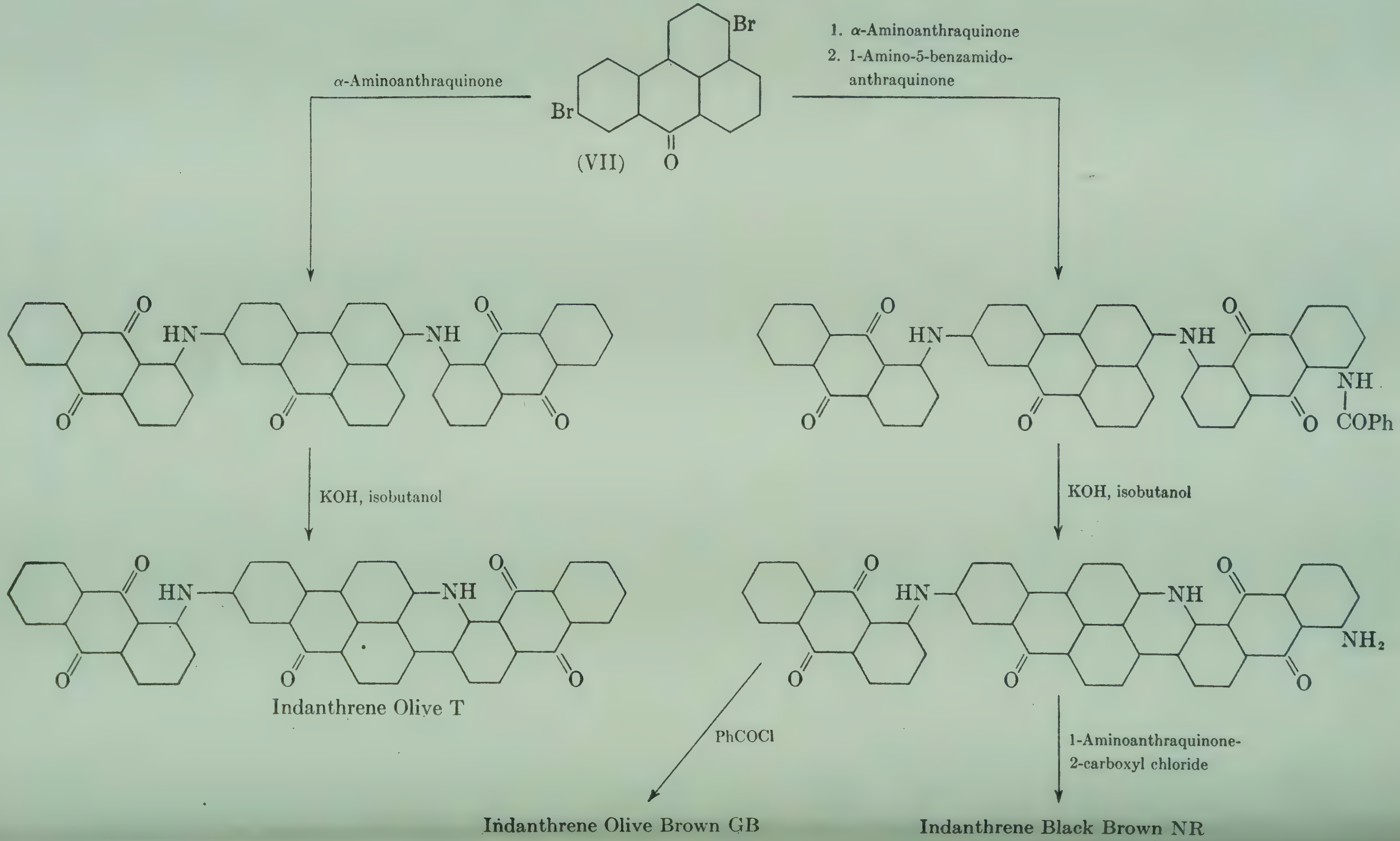
[145] IG, BP 467,919.

[145a] IG, BP 508,029.

[146] Lytle and American Cyanamid, USP 2,456,589.

CHART 6

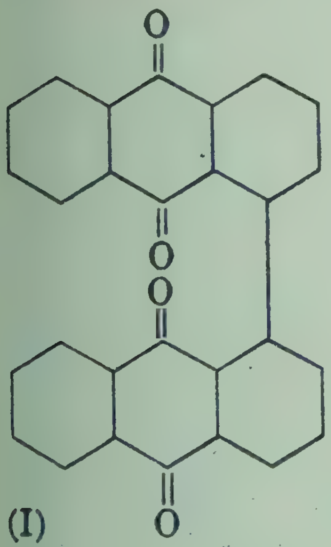
DERIVATIVES OF INDANTHRENE OLIVE GREEN


Br
Br
(VII)
O
α-Aminoanthraquinone
1. α-Aminoanthraquinone
2. 1-Amino-5-benzamido-anthraquinone
O
HN
NH
O
O
O
O
O
O
HN
NH
O
NH
COPh
O
O
O
KOH, isobutanol
KOH, isobutanol
O
HN
NH
O
O
O
O
Indanthrene Olive T
O
HN
NH
O
NH₂
O
O
O
PhCOCl
1-Aminoanthraquinone-2-carboxyl chloride
Indanthrene Olive Brown GB
Indanthrene Black Brown NR

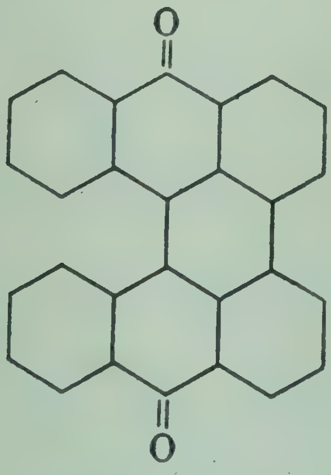
condensing (VII) with heterocyclic anthrone derivatives, such as pyrimidanthrones and pyrazolanthrones, containing a free amino group, and various minor modifications of the reactions shown in Chart 6 have been mentioned.[147] Fast gray to black vat dyes are obtained by alcoholic potash fusion of 3′,4′-phthaloyl-x-(3-benzanthronylamino)acridones, in which x can be 6, 4 or 1.[148] Gray vat dyes are obtained by condensing (VII) with a mole each of naphthostyril and an aminoanthraquinone; the latter may be a 2,1-(*N*)-anthraquinonebenzacridone.[149] By condensing 6-chloro-1-(3-benzanthronyl)aminoanthraquinone with aminoanthraquinones which may be substituted, and treating the resulting anthrimide with caustic potash, both carbazole and acridine cyclizations take place, and the products dye olive gray shades.[105] Benzanthronethiazoles and selenazoles, fused with alkali, yield black vat dyes.[151]

Miscellaneous Homocyclic Quinones

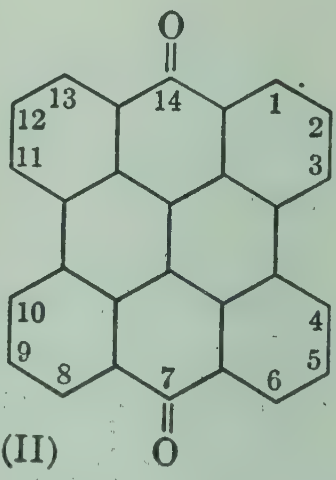
When 1,1′-dianthraquinonyl (I), which may be prepared by heating anthraquinone with antimony pentachloride in nitrobenzene or from α-aminoanthraquinone through the diazonium salt and α-iodoanthraquinone, is heated with copper and concentrated sulfuric acid, the product is *ms*-benzodianthrone or Helianthrone (Scholl, 1910), a yellow dye of no practical value.[152, 153] Treatment of Helianthrone with aluminum chloride gives *ms*-naphthodianthrone (II), which also has not been used commercially, since it requires a special method of vatting with alkali,



(I)



Helianthrone



(II)

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[147] Lycan and du Pont, USP 2,203,416; 2,111,074; 2,141,858; 2,150,093; 2,251,566; 2,312,401; 2,312,462; BP 535,789; 538,377–8.

[148] du Pont, USP 2,081,874.

[149] du Pont, USP 2,155,360.

[150] du Pont, USP 2,278,977; see also 2,188,537–8.

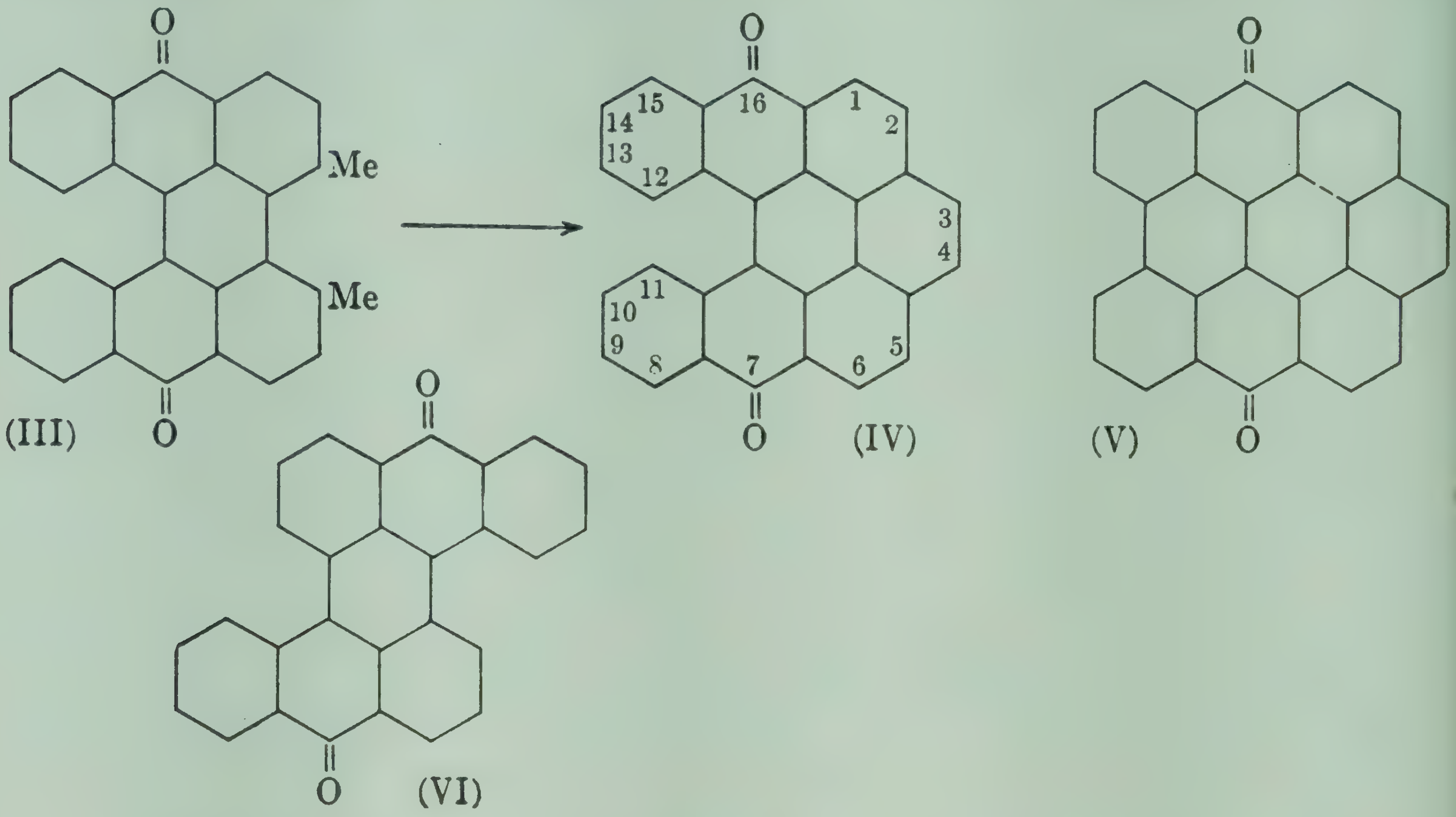
[151] du Pont, USP 2,028,114–6.

[152] Scholl and Mansfeld, *Ber.* **43,** 1734 (1910).

[153] See also Attree and Perkin, *JCS* 144 (1931); Brockmann and Mühlmann, *Chem. Ber.* **82,** 348 (1949).

hydrosulfite and zinc dust. The parent dye gives yellow shades, and by halogenation and condensation with α-aminoanthraquinone and its derivatives violet and purple dyes may be obtained.[154] The naturally occurring photodynamic pigments, hypericin and fagopyrin, are probably polyhydroxy derivatives of (II).[154a]

Alkali fusion of 3,4-dimethyl-*ms*-benzodianthrone (III) yields the orange *allo-ms*-naphthodianthrone (IV), which on baking with aluminum chloride gives the bright reddish yellow anthradianthrone (V). The light fastness of the shades is poor. By halogenation and condensation with α-aminoanthraquinones, a series of brown, red, blue, violet and black dyes have been produced. The perylene and coronene ring systems present in these polycarbocyclic quinones will be noticed. None of these dyes has found technical application, but it has been stated that halogenated (IV) and (V) have a clarity of shade approaching the basic colors, and anthradianthrone derivatives also possess excellent fastness properties, so that further syntheses in the series and careful assessment of the dyeing and fastness properties of the new vat dyes are indicated.[153]



(III) (IV) (V) (VI)

When methyleneanthrone is refluxed with alcoholic hydrochloric acid and then heated with aluminum chloride above 200° it forms a yellow compound, which on further heating at 320° evolves ethylene to give 5,6,11,12-dibenzoperylene-4,10-quinone (VI), dyeing cotton violet.[155] The dye is apparently identical with the product of the cyclization of

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[154] IG, DRP 456,583; 457,493–4; 457,687; 468,577; 468,988; 470,949; 471,039; 475,139; 485,710; 508,396; 516,399.

[154a] Brockmann *et al.*, *Chem. Ber.* **83**, 467 (1950).

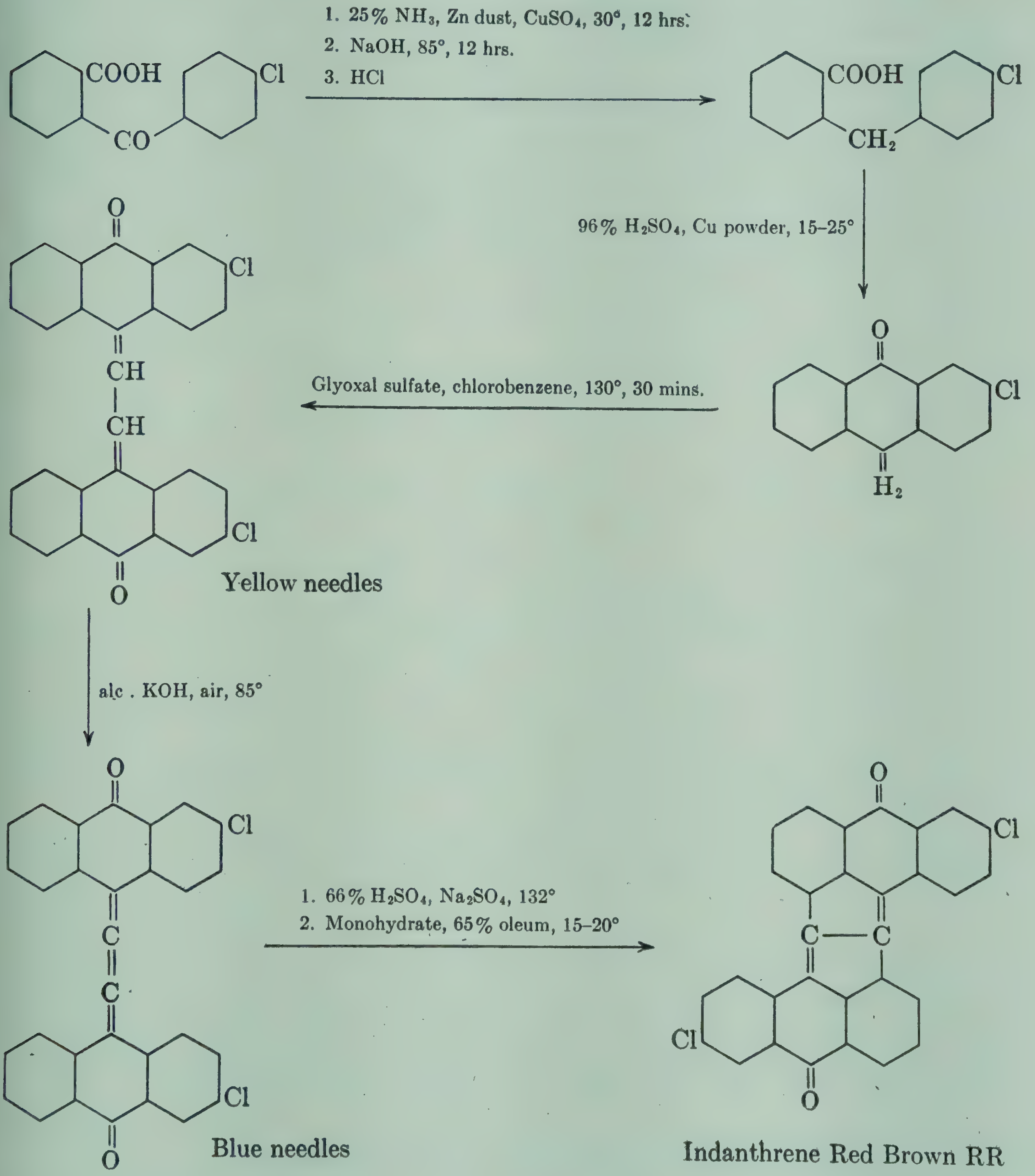
[155] IG, BP 373,129.

9,10-diphenylanthracene-1,5-dicarboxylic acid,[156] and with a dye synthesized from 1,1′-dichloro-9,9′-dianthrone.[157] The dye has poor fastness. The yellow intermediate product from methyleneanthrone, which is probably a dimeride, when heated with alkaline condensing agents, gives reddish violet substances which can be used as pigments.[65]

Acedianthrone, a new type of polycyclic quinone which is isomeric with pyranthrone and has vat dyeing properties, is obtained when two

CHART 7

Preparation of Indanthrene Red Brown RR


COOH
Cl
CO
1. 25% NH₃, Zn dust, CuSO₄, 30°, 12 hrs.
2. NaOH, 85°, 12 hrs.
3. HCl
COOH
Cl
CH₂
96% H₂SO₄, Cu powder, 15–25°
O
Cl
H₂
Glyoxal sulfate, chlorobenzene, 130°, 30 mins.
O
Cl
CH
CH
Cl
O
Yellow needles
alc . KOH, air, 85°
O
Cl
C
C
Cl
O
Blue needles
1. 66% H₂SO₄, Na₂SO₄, 132°
2. Monohydrate, 65% oleum, 15–20°
O
Cl
C
C
Cl
O
Indanthrene Red Brown RR

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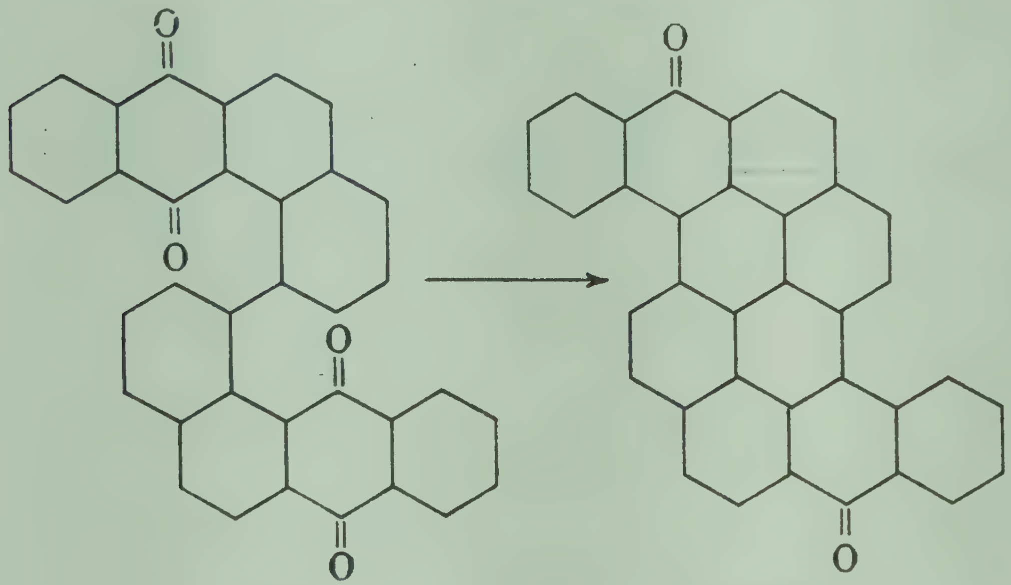
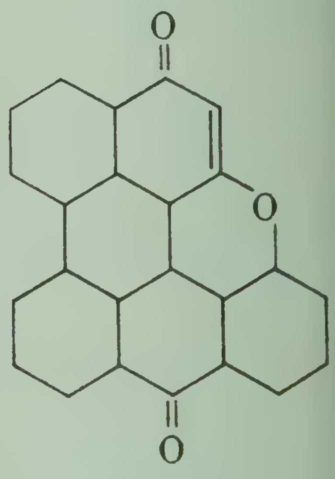
[156] Scholl, Meyer, and Winkler, *Ann.* **494,** 201 (1932).

[157] Heilbron, *Chemistry & Industry* 951 (1933).

moles of anthrone are condensed with glyoxal in the form of its sulfate, and cyclized with sulfuric acid. The dichloro derivative is Indanthrene Red Brown RR, made by the indicated series of reactions (Chart 7).[3] The vat is yellowish brown in color; in full shades the fastness to light and other agencies is excellent, but the fastness to alkali boil is of a lower degree (3–4). Condensation of the 1-chloro-9-anthrone analog of Indanthrene Red Brown RR with two moles of 1-amino-5-benzamidoanthraquinone and subsequent carbazolization give Indanthrene Brown NG, which IG produced in small quantities because of its high cost.[4a] Improved methods for the preparation of brown vat dyes from glyoxylidene-bis-anthrone or its halogen derivatives consist in heating with an organic acid halide or anhydride, an acid and an oxidizing agent, such as a mixture of acetic anhydride, sulfuric acid and nitrobenzene.[158]

Condensation of phthalic anhydride with 1,5-dihydroxynaphthalene leads to 7,15-dihydroxyhexacene-5,16,8,13-diquinone, a blue dye for cotton.[158a] The dibenzanthraquinonyl (VII) can be cyclized to a dibenzoyleneanthanthrene (VIII), which dyes violet shades on cotton, the halogen derivatives being bluer.[159]


(VII) (VIII)


(IX)

The brown vat dye (IX) is a perylene-3,10-quinone, obtained by cyclization of 1-β-naphthoxyanthraquinone and oxidation of the product.[160] A series of vat dyes, the structures of which are largely undetermined, have been prepared by Friedel-Crafts reactions on pyrene, perylene, and other complex hydrocarbons. Coronene yields vat dyes by condensation with one to three moles of phthalic anhydride in *o*-dichlorobenzene solution, and subsequent cyclization with acids.[161]

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[158] ICI, BP 551,662.

[158a] Clar and du Pont, USP 2,210,396; Clar, *Ber.* **72,** 1817 (1939).

[159] IG, BP 386,411.

[160] Clar and du Pont, USP 2,179,920.

[161] IG, BP 518,332.

Condensation of pyrene with at least two moles of phthalic anhydride or other *o*-dicarboxylic anhydride yields reddish-yellow vat dyes.[162] The reaction may be carried out in stages,[163] and pyrene has been condensed with acid chlorides to obtain di- or polyaroylpyrenes which include orange vat dyes.[164] Yellow-brown vat dyes have been obtained by fusing tetrabenzoylpyrene with potash in quinoline.[165] When perylene or one of its halogen derivatives containing at least one free peri position in each naphthalene residue is condensed with an aromatic *o*-dicarboxylic anhydride in presence of alkali-aluminum halides, fast red-brown vat dyes are produced.[166] If a large excess of the anhydride is used in this reaction the products are violet in shade.[167] Fluoranthene has been condensed with phthalic anhydride under conditions in which at least 2½ moles of the latter enter into the reaction, and the product is a fast yellow vat dye.[168] Pyrene and chrysene have found application in the production of vat dyes in another manner. Halogenated pyrenequinones are condensed with compounds such as primary and secondary amines to obtain olive, brown, green, blue or violet vat dyes.[169] Halogenated *o*-chrysenequinones similarly yield brown, red-brown, bordeaux, corinth, and gray dyes,[170] which may be modified by treatment with cyclizing agents, yielding olive and brown vat dyes.[171]

1,9-Heterocyclic Derivatives of Anthrone

Flavanthrones

Bohn (1901) noticed that when the temperature of fusion of β-aminoanthraquinone with caustic potash to produce indanthrone was raised to 300–350°, the shades became greener and a yellow dye could be isolated, in addition to the blue indanthrone. It was then found that a technically feasible process for the preparation of the yellow dye, although the yield was less than 30%, was to heat the amine with antimony pentachloride in nitrobenzene solution,[172] and it was marketed under the name of Flavanthrene (later, Indanthrene Yellow G; CI 1118), simultaneously

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[162] Ciba, BP 466,968.

[163] Ciba, BP 469,638.

[164] Ciba, BP 459,333.

[165] Scholl and Meyer, Ciba BP Appl. 19,862.

[166] IG, DRP Anm. J. 51,273.

[167] IG, DRP Anm. J. 51,966.

[168] Ciba, BP 468,648. See also Ref. 19.

[169] Ciba, BP 447,890.

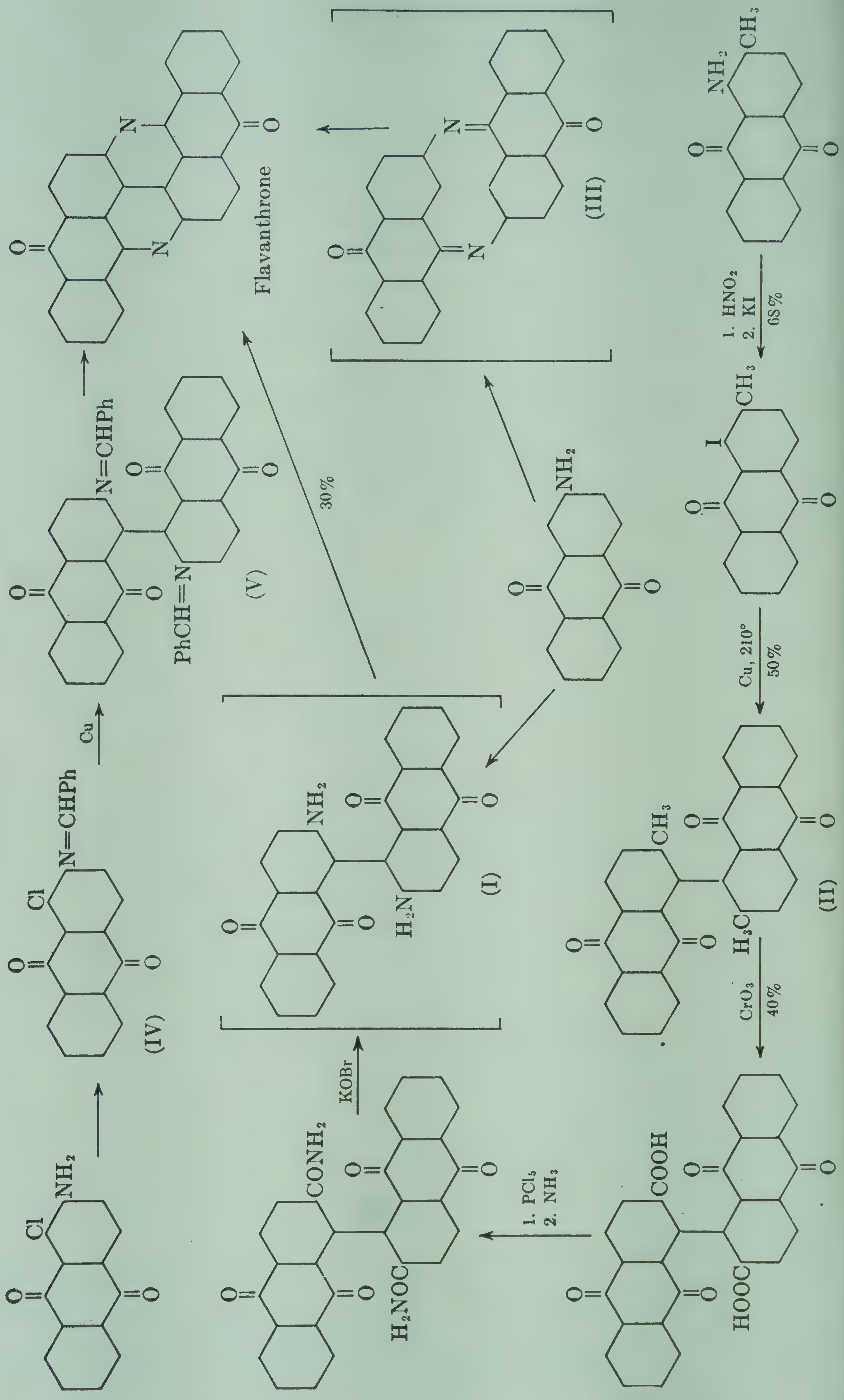
[170] IG, BP 451,875. See also Ref. 20.

[171] IG, DRP Anm. J. 50,915.

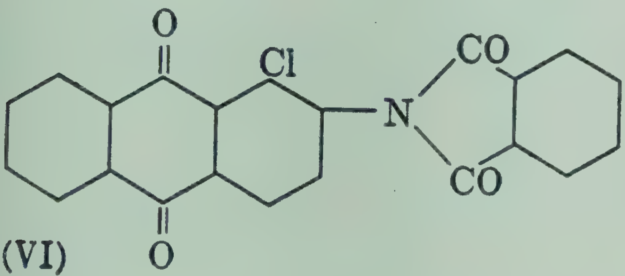
[172] BASF, DRP 138,119. Titanium tetrachloride at 100–175° gives flavanthrone in excellent yield; American Cyanamid, USP 2,468,599.

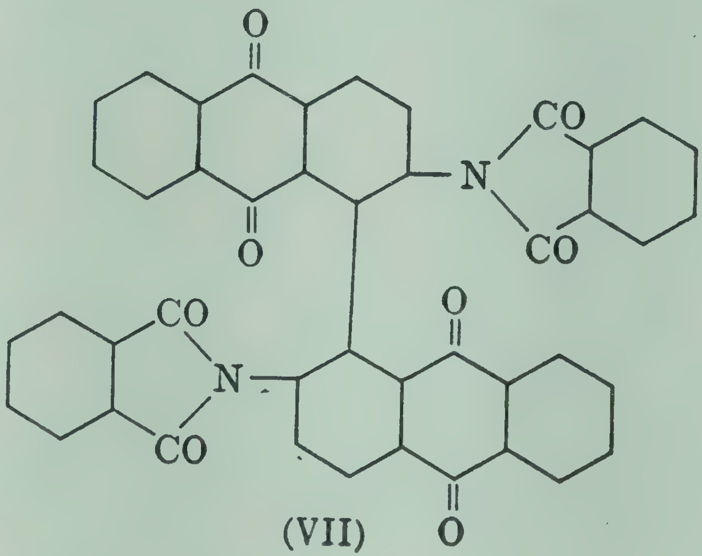
CHART 8

SYNTHESES OF FLAVANTHRONE


Cl
NH$_2$
(IV)
N=CHPh
Cu
PhCH=N
(V)
Flavanthrone
30%
CONH$_2$
H$_2$NOC
KOBr
(I)
H$_2$N
(III)
1. PCl$_5$
2. NH$_3$
COOH
HOOC
CrO$_3$
40%
H$_3$C
CH$_3$
(II)
Cu, 210°
50%
I
1. HNO$_2$
2. KI
68%

with Indanthrene Blue. As for indanthrone, flavanthrone is to be preferred to flavanthrene as a chemical name. The probable mechanism of the reaction involves two stages: the oxidation of β-aminoanthraquinone to the diaminodianthraquinonyl (I) and dehydration of (I) to flavanthrone (see Chart 8).[173] The first stage of the self-condensation of β-aminoanthraquinone, however, might conceivably be the formation of the bis-ketimine (III). Starting from 2-methylanthraquinone and proceeding through the indicated stages, Scholl was able to demonstrate the constitution of flavanthrone by a synthesis in which the formation of a 1,1′-dianthraquinonyl derivative definitely preceded the cyclization to the dye. In the course of this work, Scholl found that alkali fusion of (II) gave a new orange dye, pyranthrone. The constitution of flavanthrone has been further confirmed by Ullmann's method for its production,[174] of which the present IG process is a modification. In the Ullmann synthesis 1-chloro-2-aminoanthraquinone is converted into the Schiff's base (IV), which on heating with copper yields the dianthraquinonyl (V); the action of sulfuric acid then yields flavanthrone by hydrolysis and cyclization. In this manner derivatives of flavanthrone (e.g. a dimethoxy compound which is a red dye) can also be prepared.[175] In the IG process[2, 176] 1-chloro-2-aminoanthraquinone (210 kg.) is heated with phthalic anhydride (132) and sublimed ferric chloride (4.4) in trichlorobenzene (170) at 215–230°. Water and solvent distil over, aided by a current of nitrogen, and when the distillate is about 100 kg. the residue is heated at 230° for 5 hours. The phthalimide (VI) thus formed is not isolated, and is converted directly into the dianthraquinonyl (VII). After removing water completely by adding and distilling off more


(VI)


(VII)

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[173] Scholl, *Ber.* **40,** 1691 (1907); **41,** 2304 (1908); **43,** 1740 (1910); Schwenk, *Chem. Ztg.* **52,** 45, 62 (1928). See also Chapter XXXI under indanthrone.

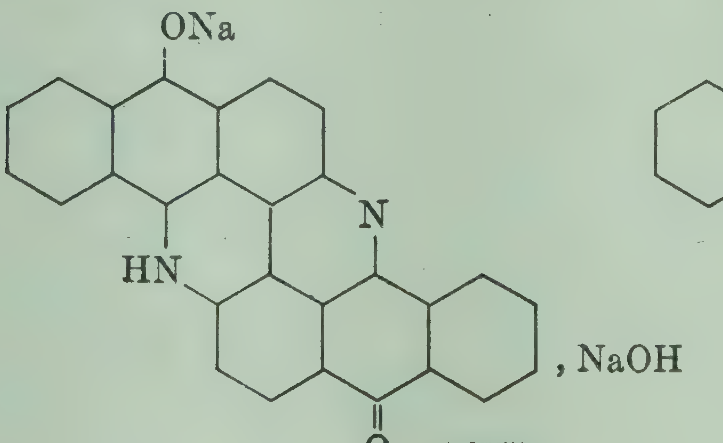
[174] Ullmann, DRP 248,999.

[175] IG, DRP 456,584.

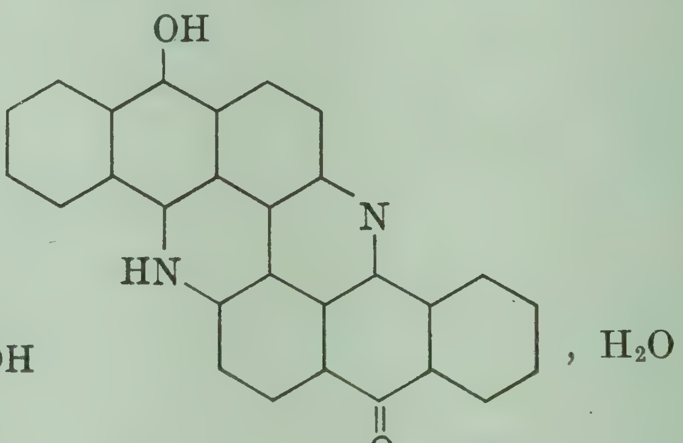
[176] Wawiasky *et al.*, IG, DRP 558,474; 560,237.

trichlorobenzene, copper powder (80 kg.) is added, and the mixture is refluxed for several hours. On cooling to 130° by adding fresh trichlorobenzene, the product is filtered in a pressure filter and washed with hot trichlorobenzene. The product (VII) contains copper, which is removed by heating at 90° for 3 hours with water (1000 kg.), 30% hydrochloric acid (420) and sodium chlorate (33). The residue, filter-pressed and washed, is hydrolyzed to (I) and cyclized to flavanthrone in one process by boiling with water (3500) and 40°Be caustic soda solution (620) for 6 hours.

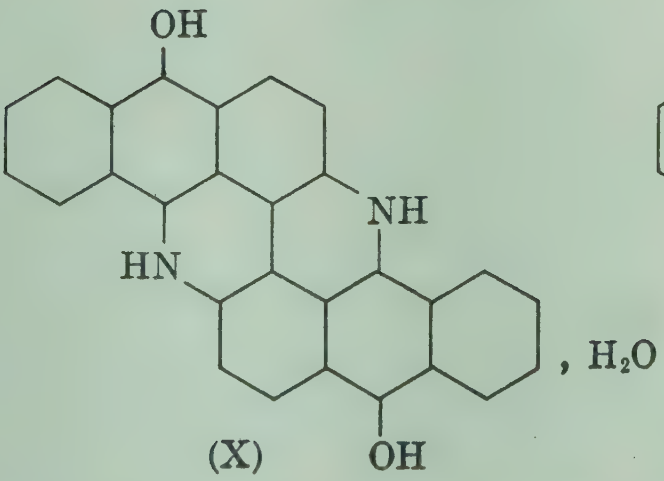
The normal alkaline hydrosulfite vat of flavanthrone is blue in color. This profound color change of yellow to blue is utilized in testing for the presence of an excess of reducing agent in vat dyeing and other processes involving alkaline reduction; vat paper used for this purpose is filter paper dyed yellow with flavanthrone. More drastic reduction of flavanthrone gives a brown vat, which undergoes reoxidation very readily, and the constitution of the blue and brown reduction products has been debated. Scholl[177] has shown that the reduction can be carried out in several stages, the alkali salts of the dihydro, tetrahydro, and hexahydro derivatives being formed successively. Since the dihydro compound formed a disodium salt, but only a monobenzoyl derivative, Scholl assigned the structure (VIII) to the blue vat. The tendency of flavanthrone and its derivatives to form stable hydrates supported the



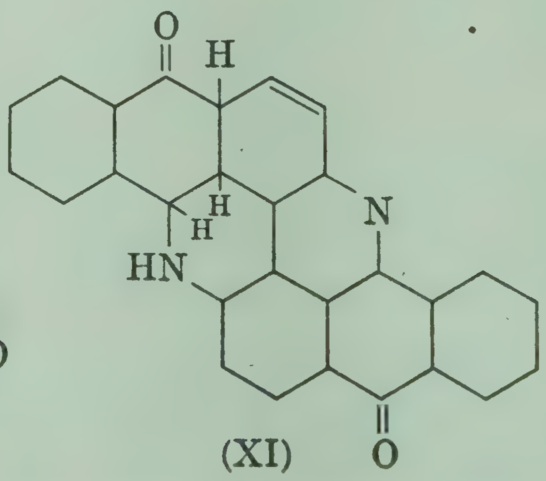
(VIII)



(IX)



(X)



(XI)

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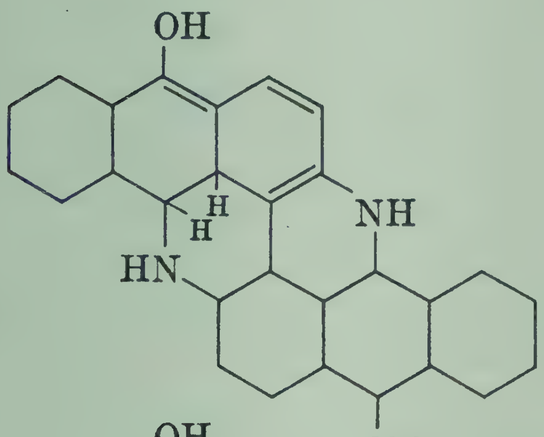
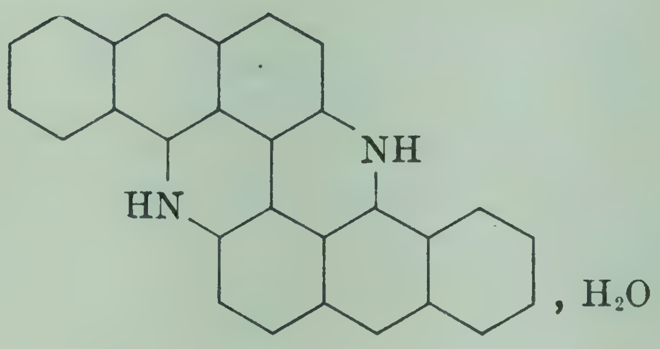
[177] Scholl, *Ber.* **40,** 933 (1907); **41,** 2304 (1908); Scholl and Neovins, *ibid.* 2534; Scholl and Edlbacher, *ibid.* **44,** 1727 (1911).

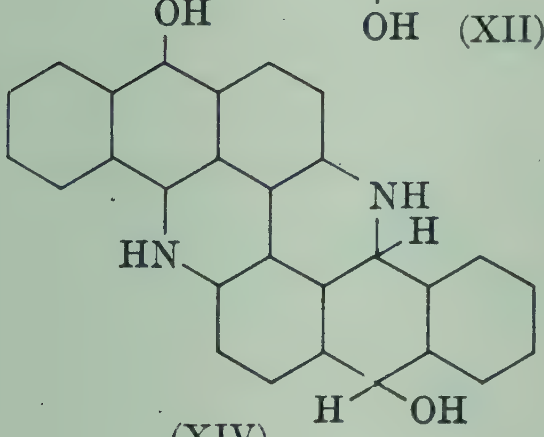
suggested coordination of a mole of sodium hydroxide. The leuco acid monohydrate (IX) separates as bluish green flocks on the addition of acetic acid; the mole of water is lost only on heating at 150–170°. The change in shade from yellow to green produced by the action of strong sunlight on cotton dyed with flavanthrone is probably due to the formation of the leuco acid (IX). The basicity of the unreduced pyridine ring in (IX) enables it to form a hydrochloride. Reduction of flavanthrone with zinc dust and caustic soda at 70–80° in an atmosphere of hydrogen gives α-tetrahydroflavanthrone (X) which is dark greenish blue in color, together with a little of the α-hexahydro derivative. Phosphorus and hydriodic acid at 140–190° convert flavanthrone into β-tetrahydroflavanthrone (XI), a green substance, which turns into a red enolic modification on treatment with alkalis. β-Hexahydroflavanthrone (XII) is obtained as an unstable yellow solution from (XI), caustic soda and zinc dust. By the prolonged action of red phosphorus and hydriodic acid on flavanthrone at 210° flavanthrine hydrate (XIII) is produced; flavanthrone is regenerated from (XIII) by oxidation in concentrated sulfuric acid. Reduction of flavanthrone with caustic soda solution and zinc dust, until the blue vat changes in color to green, brown and finally red with a brown precipitate, leads on acidification with acetic acid to the monohydrate of α-hexahydroflavanthrone (XIV) as a black-blue powder. At 300° in carbon dioxide the hydrate forms anhydrous (XIV), and subsequently flavanthrinol (XV). Oxidation regenerates flavanthrone from all these compounds.



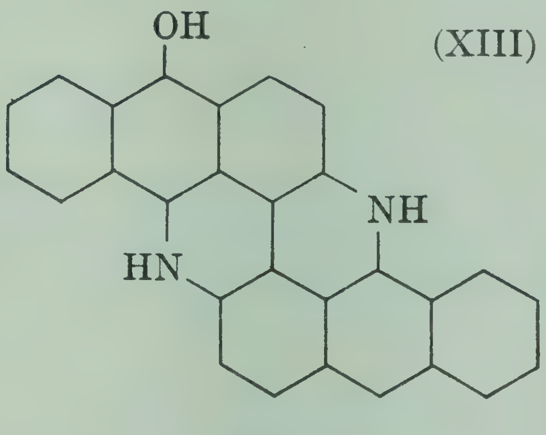
(XII)



(XIII)

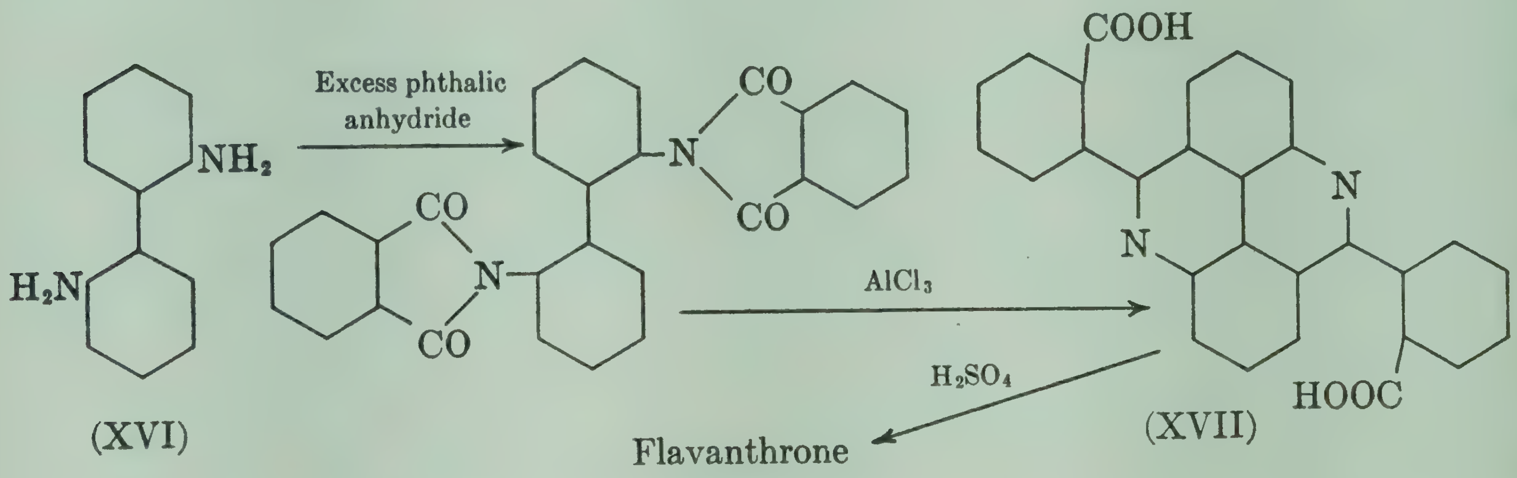


(XIV)

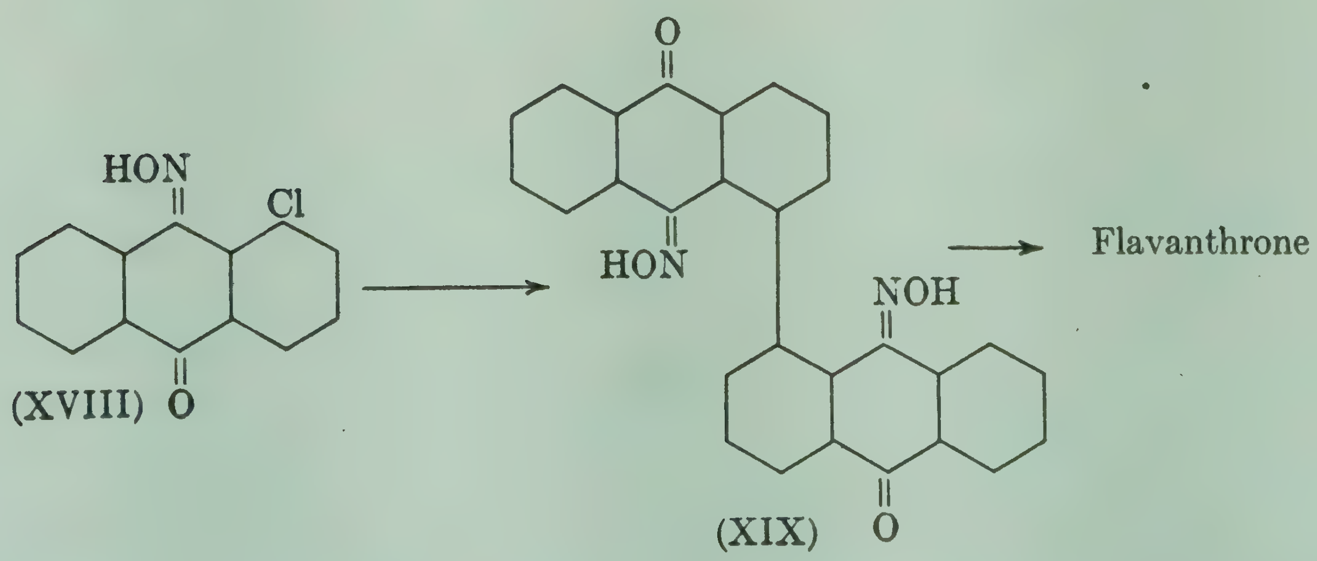


(XV)

Flavanthrone (Indanthrene, Caledon, Paradone, Carbanthrene, Ponsol Yellow G), which dyes orange-yellow shades from the blue vat, continues to be an important dye (partly because it is a nontenderer and has good light fastness), although the fastness to alkali boil is poor (2) as a result of the reducibility of the dye by cellulose and boiling alkali, and the dye is therefore not recommended for goods which are to be bleached after dyeing. The oxidation of the leuco compound to the parent dye takes place rather slowly, and treatment with a weak solution of dichromate and sulfuric acid or with perborate is recommended, particularly in machine dyeing. By the introduction of halogen in the 3,3′-positions the fastness is improved, but the shades are redder and less attractive. The dibromo compound was formerly marketed as Indanthrene Yellow R (ST 1242). Alizanthrene Orange (British Alizarin Co.; CI 1119), no longer marketed, was dibromoflavanthrone prepared by the action of antimony pentachloride in nitrobenzene on 2-amino-3-bromoanthraquinone.



An interesting synthesis of flavanthrone starts from 2,2′-diaminodiphenyl (XVI) and proceeds through the 4,9-diazapyrene derivative (XVII).[6,178] Another synthesis is by the action of copper on 1-chloro-



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[178] IG, BP 431,790.

anthraquinone-9-oxime (XVIII), and subsequent cyclization of the dianthraquinonyl (XIX).[179]

PYRAZOLANTHRONES

1-Anthraquinonylhydrazine cyclizes readily to pyrazolanthrone (I),[180] and alkali fusion of (I) results in the union of two molecules and the formation of a dye, Pyrazolanthrone Yellow (see Chart 9) (CI 1122), which is now obsolete;[181] the fastness to alkali is poor because of the two acidic hydrogen atoms. Alternative structures (e.g., IIA and III) were at one time suggested for Pyrazolanthrone Yellow and its derivatives, but it has now been shown that the dimerization of pyrazolanthrone merely consists in the formation of a diaryl linkage in the 2,2′-positions of the anthrone residues. This has been confirmed by a synthesis of Pyrazolanthrone Yellow by the action of copper on an *N*-acyl derivative of 3-bromo-1,9-pyrazolanthrone (II) which is obtained by diazotizing 2-bromo-1-aminoanthraquinone, reducing to the hydrazine under conditions in which the halogen is not removed, and cyclizing to the pyrazole.[182]

Replacement of the acidic hydrogen atoms by ethyl groups in Pyrazolanthrone Yellow leads to more useful dyes, Grelanone Red 2B (GrE, 1924) (Indanthrene Rubine R; see Chart 9) and Grelanone Scarlet G; the latter is probably the monoethyl compound.[183] Indanthrene Rubine R has also been assigned the structure of an *N*,*N*′-diethyl derivative of (IIA).[4a]

Replacement of one or both of the alkyl groups of bis-*N*-alkylpyrazolanthronyls by an alkoxyalkyl group such as β-methoxyethyl yields improved red vat dyes; the solubility of the leuco compounds and fastness to soaping are improved, while the shade may be yellower.[184] Bright red to bluish red dyes are obtained by introducing in the parent 1-hydrazinoanthraquinone a methoxyl group at 4–8, an aldehyde group at 6 or 7, or a 6-chlorine atom.[185]

Self-condensation of (II) by means of copper and potassium acetate leads to the complex polycyclic dye (III), which gives fast red shades from a blue vat.[186] The condensation of (I) with 3-bromobenzanthrone in presence of potassium carbonate at 190–195° gives the benzanthronyl-

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[179] IG, DRP Anm. J. 44,188; 44,995.

[180] Schmidt and Bayer, DRP 163,447; 171,293.

[181] GrE, DRP 255,641; IG, DRP 457,182; Mayer and Heil, *Ber.* **55,** 2155 (1922).

[182] Lüttringhaus *et al.*, USP 1,817,995.

[183] GrE, DRP 359,139; IG, DRP 458,538.

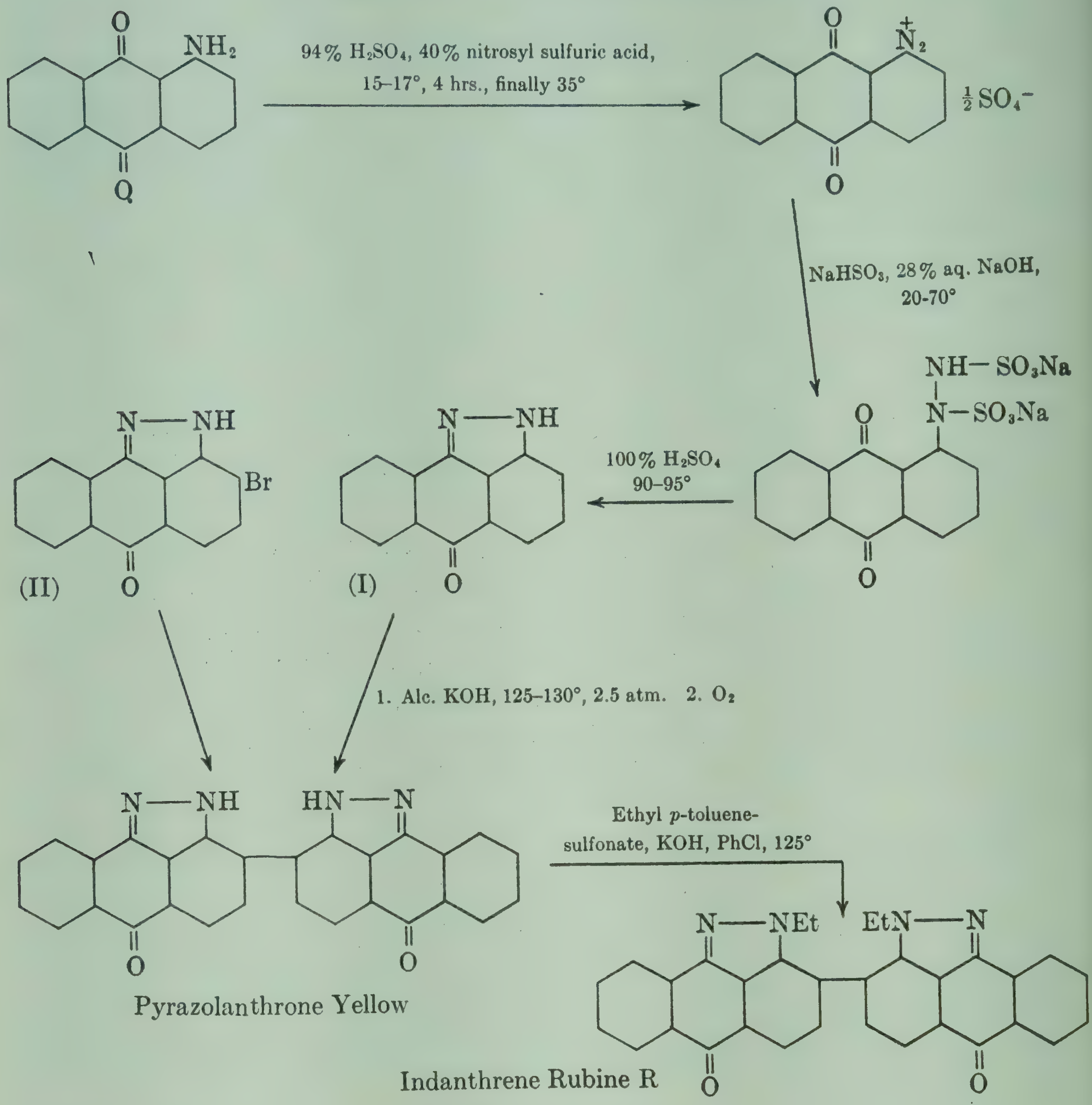
[184] Ciba, BP 469,491; IG, BP Appl. 14,638/36. According to Ref. 76*a*, Cibanone Red 2B, which is not in the current Cibanone shade card, is of this type.

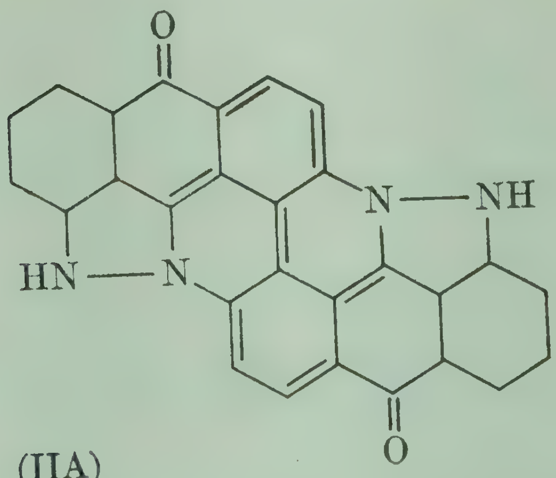
[185] Du Pont, USP 2,155,364; 2,155,369; 2,162,201; 2,162,205–6.

[186] IG, BP 285,555.

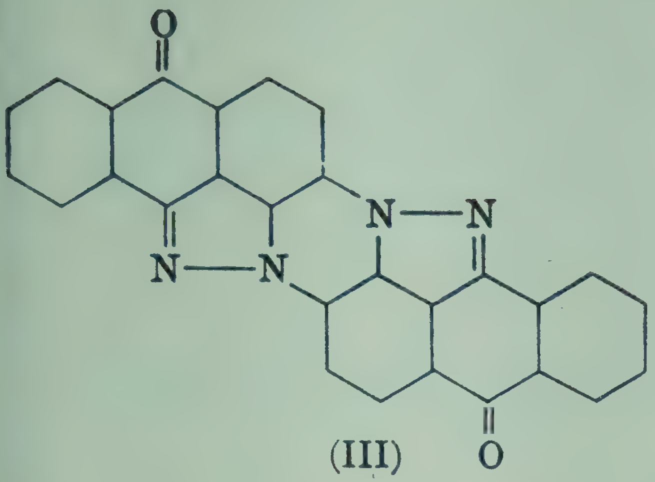
CHART 9

PREPARATION OF INDANTHRENE RUBINE R

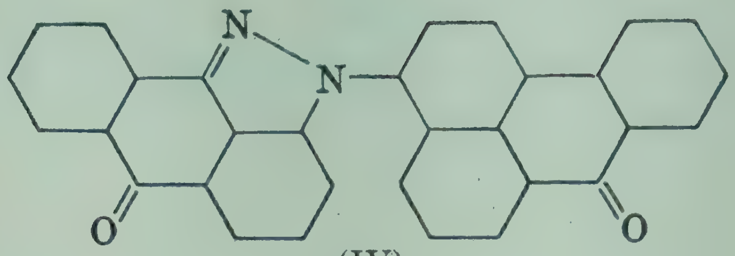

O
NH₂
Q
94% H₂SO₄, 40% nitrosyl sulfuric acid,
15–17°, 4 hrs., finally 35°
O
N₂ +
½ SO₄⁻
O
NaHSO₃, 28% aq. NaOH,
20-70°
NH—SO₃Na
N—SO₃Na
O
O
100% H₂SO₄
90–95°
N—NH
O
(I)
N—NH
Br
O
(II)
1. Alc. KOH, 125–130°, 2.5 atm. 2. O₂
N—NH
HN—N
O
O
Pyrazolanthrone Yellow
Ethyl p-toluenesulfonate, KOH, PhCl, 125°
N—NEt
EtN—N
O
O
Indanthrene Rubine R



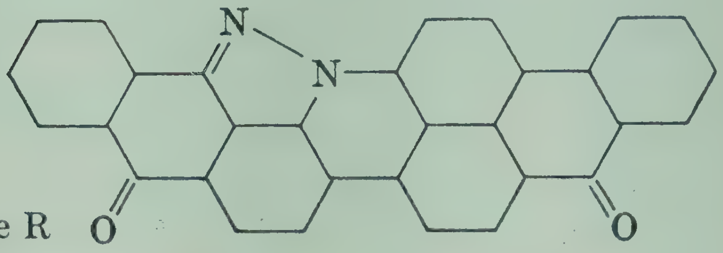
(IIA)



(III)



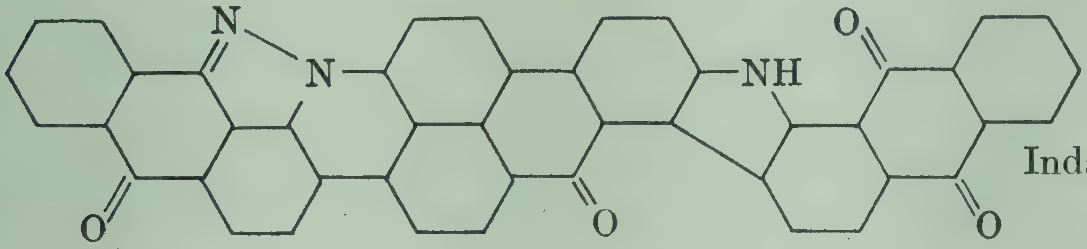
(IV)



Indanthrene Navy Blue R

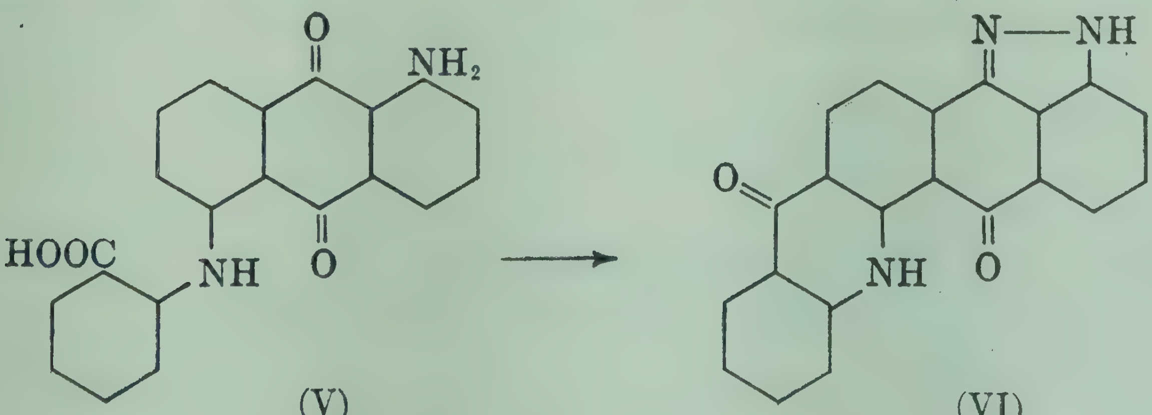
pyrazolanthrone (IV), which on heating with alcoholic potassium hydroxide at 90–95° for a few hours cyclizes to Indanthrene Navy (or Marine) Blue R (Wilke, 1931).

The introduction of an anthraquinonylamino group in Indanthrene Navy Blue R leads to a gray dye, Indanthrene Gray M, which has excellent fastness to all agencies. It is prepared by condensing 3,9-dibromobenzanthrone with one mole of pyrazolanthrone as for Indanthrene Navy Blue R, and then with one mole of α-aminoanthraquinone in presence of copper chloride; the final stage is cyclization to a pyrazole-acridine-carbazole by means of alcoholic potash. Indanthrene Gray MG is a purer brand of Gray M, prepared by using purified dibromobenzanthrone.[4a] Indanthrene Navy Blue R and Gray M have light fastness 6–8, chlorine fastness 4–5, and soda-boil fastness 3–4.

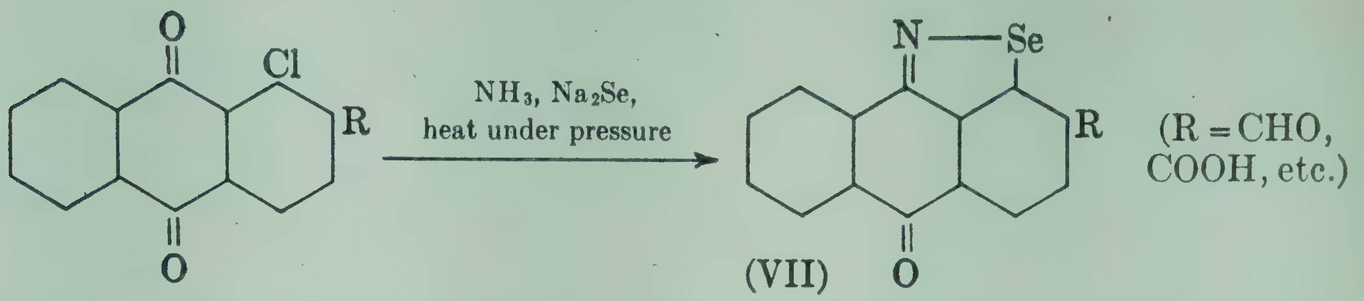


Indanthrene Gray M

Pyrazolanthrone and acridone cyclizations to form (VI) occur simultaneously when 1-amino-5-anilinoanthraquinone-2′-carboxylic acid (V) is diazotized in sulfuric acid, the isolated diazonium sulfate reduced with



(V) (VI)

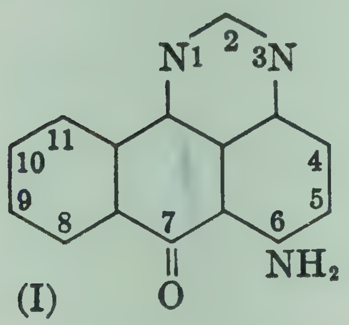


(VII)

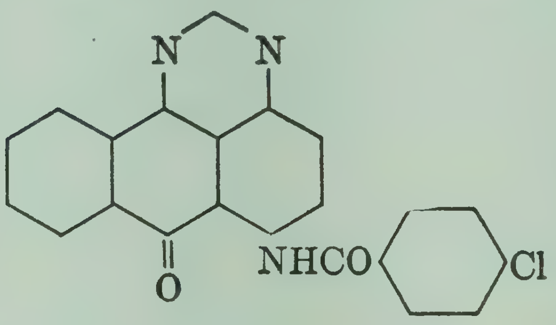
sodium sulfite, and the hydrazine heated with 96% sulfuric acid.[187] Dyes derived from selenazolanthrone (VII) have been described.[188]

PYRIMIDANTHRONES

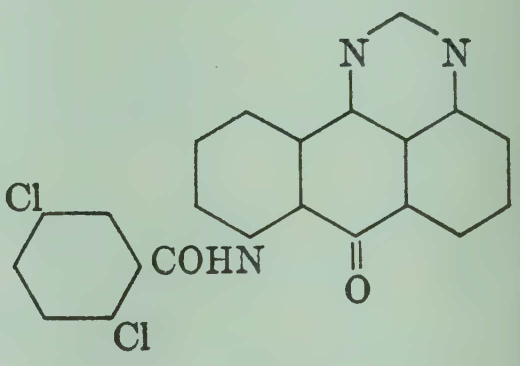
Although 1,9-pyrimidanthrones, such as the 6-amino derivative (I), have been known for a long time,[189] as well as the vat dyeing properties of the benzoyl derivatives of (I) and the 8-isomer, vat dyes of this type were only included in the commercial range more recently (1934); there are two representatives, Indanthrene Yellow 4GK and 7GK.[2, 190] The relevant patents[191] appeared in 1932–34. These dyes are remarkable for two reasons. The pyrimidine ring system has the specific effect of imparting to the dyes the valuable property of not tendering cellulose when acted upon by light or by oxidizing agents—a serious defect of many of the yellow and orange dyes of the anthraquinone series.[192] As vat dyes the pyrimidanthrones are unique in their possession of a single carbonyl group. As stated earlier,[193] an anthrone derivative, such as benzanthrone or an amino- or benzamido-benzanthrone, does not have vat dyeing properties unless the molecule is doubled by appropriate methods of condensation, so that the compound contains a pair of carbonyl groups connected by a conjugate chain and forms a quinonoid system. The vattability of pyrimidanthrone is due to the increase in



(I)



Indanthrene Yellow 7GK



Indanthrene Yellow 4GK

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[187] Stilmar and du Pont, USP 2,270,354.

[188] Lulek, and du Pont, USP 2,049,212.

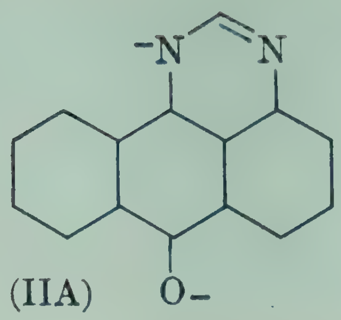
[189] Bayer, DRP 220,314.

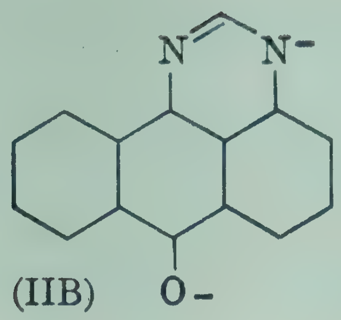
[190] Sunthankar, *Proc. Indian Acad. Sci.* **32A,** 240 (1950).

[191] Kunz, Köberle, and IG, DRP 573,556; 633,207; BP 385,295.

[192] See also Chapter XL.

[193] See Chapter XXX.

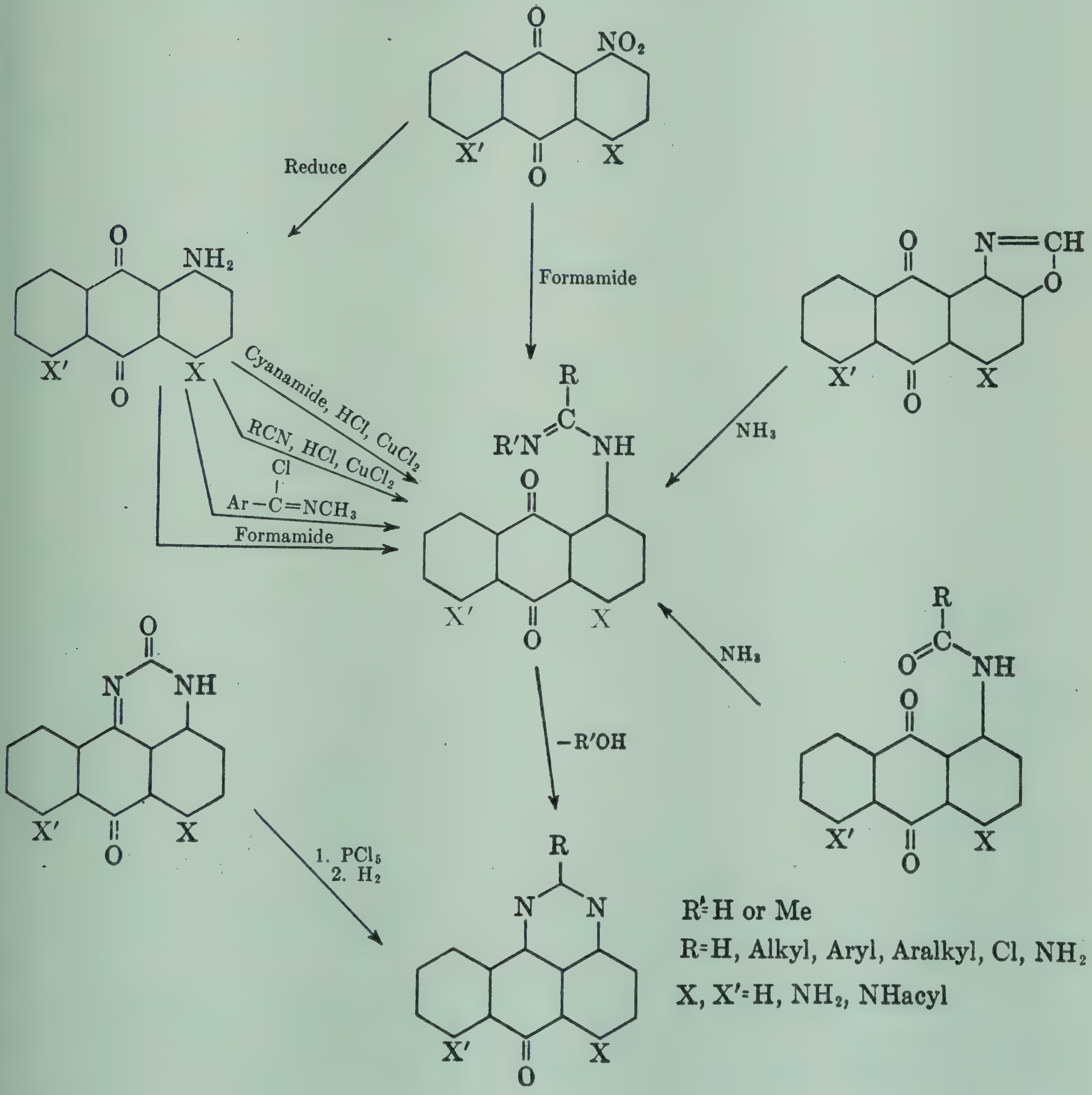

(IIA)


(IIB)

acid strength of dihydropyrimidanthrone by the resonance stabilization of the anion as indicated in structures (IIA) and (IIB).[192] Pyrimidanthrone therefore forms an alkali-soluble leuco derivative on reduction, and when a benzamido group is present, the affinity of the leuco compound for cellulose becomes adequate for dyeing purposes.

CHART 10

SYNTHESES OF PYRIMIDANTHRONES


Reduce
Formamide
Cyanamide, HCl, CuCl₂
RCN, HCl, CuCl₂
Ar−C(Cl)=NCH₃
Formamide
NH₃
NH₃
−R′OH
1. PCl₅
2. H₂

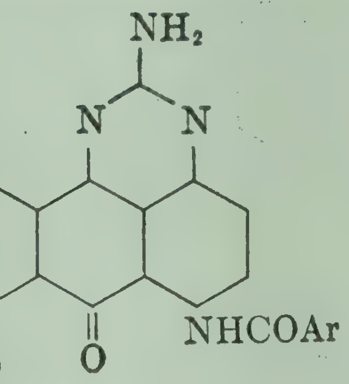
R′=H or Me

R=H, Alkyl, Aryl, Aralkyl, Cl, NH₂

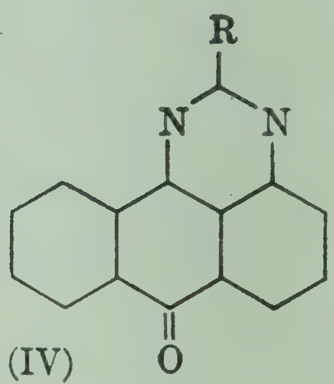
X, X′=H, NH₂, NHacyl

6-Aminopyrimidanthrone (I) is prepared in 80% yield by heating 1,4-diaminoanthraquinone (0.5 part), 30% ammonia (1), 30% formaldehyde (1) and Ludigol (sodium *m*-nitrobenzenesulfonate; 0.375) in an autoclave at 88–92° for 15 hours.[2] A nearly quantitative yield of the 8-amino compound is obtained by heating 1,5-diaminoanthraquinone-2-sulfonic acid (1.1 part) with formamide (5) and nitrobenzene (0.2) for 13 hours at 140–145°, and subsequent hydrolysis of the sulfonic group by means of hot alkaline hydrosulfite.[2] In view of the remarkable property of the pyrimidine nucleus in rendering yellow and orange anthraquinonoid vat dyes free from the danger of accelerating the action of light on cellulose, several routes to the pyrimidanthrones have been developed by IG (see Chart 10).[6, 194]

1-Amino-4 or 5-aroylamidoanthraquinones heated with cyanamide and hydrochloric acid yield 2-amino-6 or 8-aroylamidopyrimidanthrones (e.g. III), which may be acylated to give yellow and orange dyes.[195] α-Aminoanthraquinones may be condensed with nitriles in presence of aluminum chloride to obtain 2-substituted pyrimidine derivatives (IV).[196]



(III)



(IV)

Anthrimides, and the corresponding carbazoles by the usual cyclization methods, can be prepared by condensing aminopyrimidanthrones with α-chloroanthraquinones, or 6- and 8-bromopyrimidanthrones with α-aminoanthraquinones. In the former case, 8-aminopyrimidanthrone is preferably employed, since the 6-isomer (I) reacts with halogenoanthraquinones only with difficulty. A series of violet, blue, gray and black dyes can be prepared in this manner, and they are characterized by their high tinctorial power, excellent fastness to light and wet treatments, and suitability for printing. Thus the replacement of α-aminoanthraquinone by 8-aminopyrimidanthrone in condensations leading to vat dyes (e.g., the preparation of Indanthrene Direct Black RB and Indanthrene Olive Green B) yields analogous dyes with considerably augmented color value and fastness;[6] by using simpler aliphatic or

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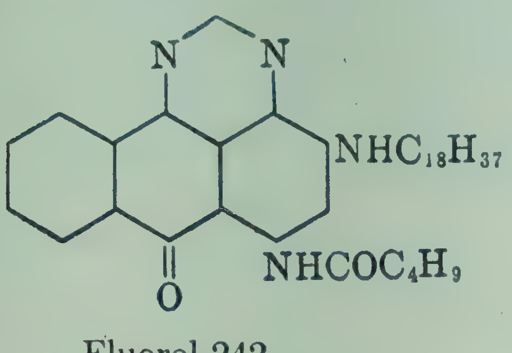
[194] IG, DRP 566,474; Kunz, Köberle, and IG, DRP 595,097; 595,903; 633,564.

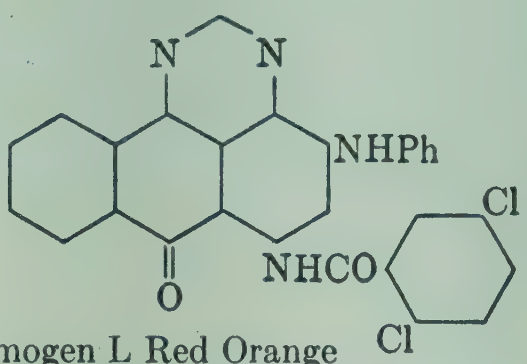
[195] IG, DRP Anm. J. 46,782.

[196] IG, BP 415,069.

aromatic compounds, dyes for acetate silk or intermediates for acid wool dyes have been obtained.[197, 198]



Fluorol 242

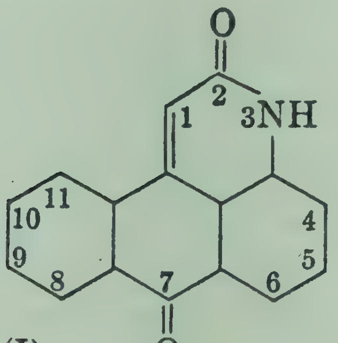


Lumogen L Red Orange

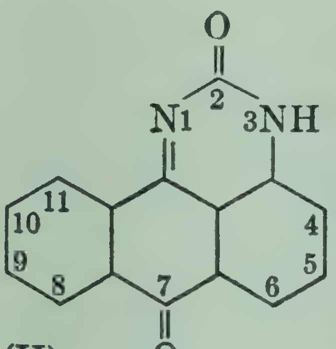
Some pyrimidanthrone derivatives (e.g. Fluorol 242) exhibit a strong fluorescence and may be used for coloring petroleum fractions and similar purposes. Lumogen L Red Orange is a pyrimidanthrone derivative useful as a luminescent dye.[2]

ANTHRAPYRIDONES AND ANTHRAPYRIMIDONES

Anthrapyridones (I) and anthrapyrimidones (II), which are 10-anthrone derivatives with a pyridone or pyrimidone ring fused in the 1,9-positions, do not possess vat dyeing properties unless anthraquinone-carboxylamido or anthrimide groups are present, and the anthrapyridone and anthrapyrimidone systems are more useful for the production of acid dyes.[198] Among the commercial vat dyes an example is Algol Red BTK (Algol Red B; ST 1261, CI 1155), which dyes pleasant rose shades, but is now obsolete; it is prepared by the indicated series of reactions.



(I)



(II)

6-Amino-3-methylanthrapyridone (III), condensed with 6- and 7-bromo-2-*p*-chlorophenylanthraquinone, gives fast bluish red dyes.[199] Condensation products of (III) or of aminoanthrapyrimidones with an anthraquinone-2-carboxyl chloride are yellowish to bluish-red dyes.[200] The anthrapyridone-acridone (IV) is a violet dye.[200a]

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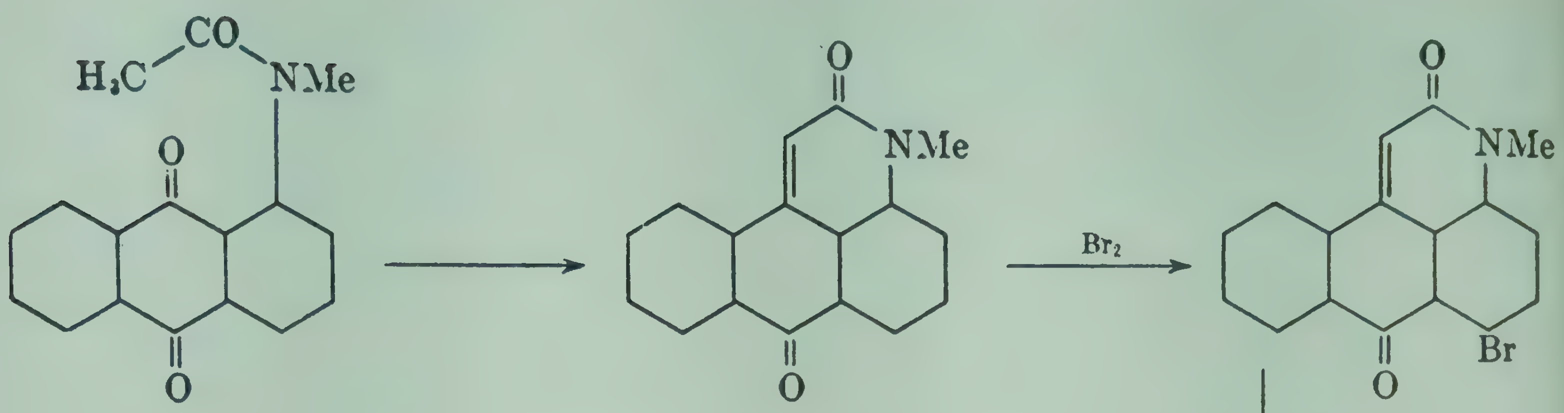
[197] IG, BP 407,363.

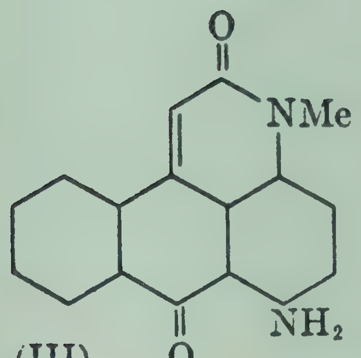
[198] See Chapter XXIX. See also IG, DRP 621,455; 633,308; 655,650; 658,114; 659,234.

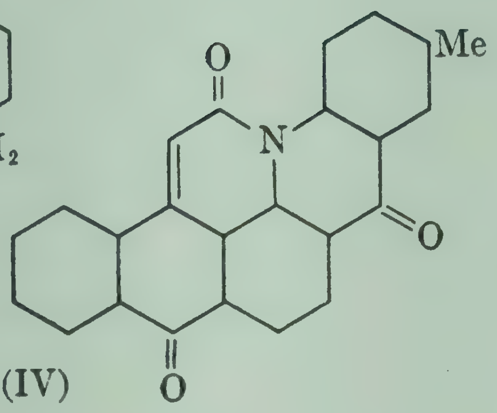
[199] Wuertz, Rintelman, and du Pont, USP 2,204,741–2.

[200] IG, BP 354,943.

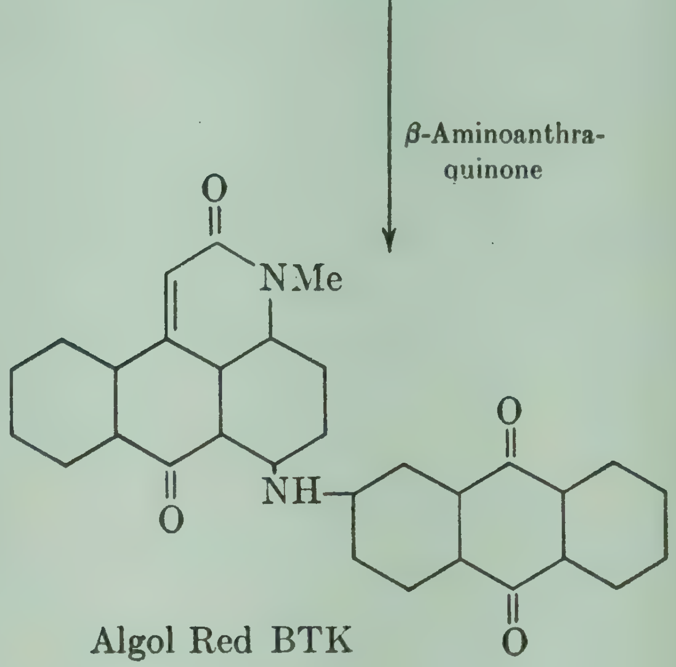
[200a] Lukin and Aronovich, *J. Gen. Chem.* (*U.S.S.R.*) **19,** 358 (1949).




(III)



(IV)



Algol Red BTK

Miscellaneous Heterocyclic Compounds

In extension of their work on yellow vat dyes containing pyridine and pyrimidine rings, IG have made a systematic investigation of the influence of the pyridine nucleus in vat dyes on color and dyeing properties.[6, 201] The preparation of a large number of derivatives of azabenzanthrone (e.g. I) corresponding to known benzanthrone dyes[202] has been described. The products include violet, blue, olive-green and gray vat dyes.[203] Pyridinobenzanthrones of the type (II) can be made from aminobenzanthrones by the Skraup synthesis; (II) by potash fusion gives a blue vat dye. In dipyridinoanthanthrone (yellow) and -mesoanthradianthrone (bluish red) the pyridine nuclei have little effect on shade.[204]

1′,2′-Benz- and 1′(*N*),2′-pyridinopyrene, like pyrene itself, yield on oxidation a mixture of *cis* and *trans* quinones, and ultimately break down to benzanthrone- and 11-azabenzanthrone-3,4-dicarboxylic anhydrides respectively. The latter has been converted into orange imidazole dyes and also decarboxylated to 11-azabenzanthrone (I).[5]

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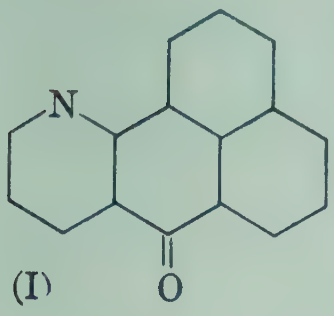
[201] See also IG, BP 406,008; 407,194; DRP Anm. J. 51,855.

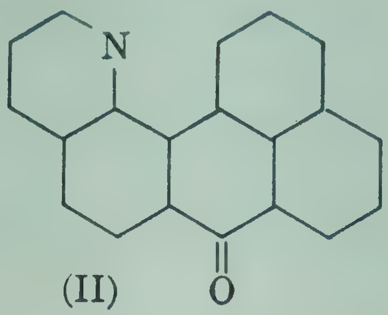
[202] IG, FP 753,828.

[203] IG, BP 444,812; 450,244.

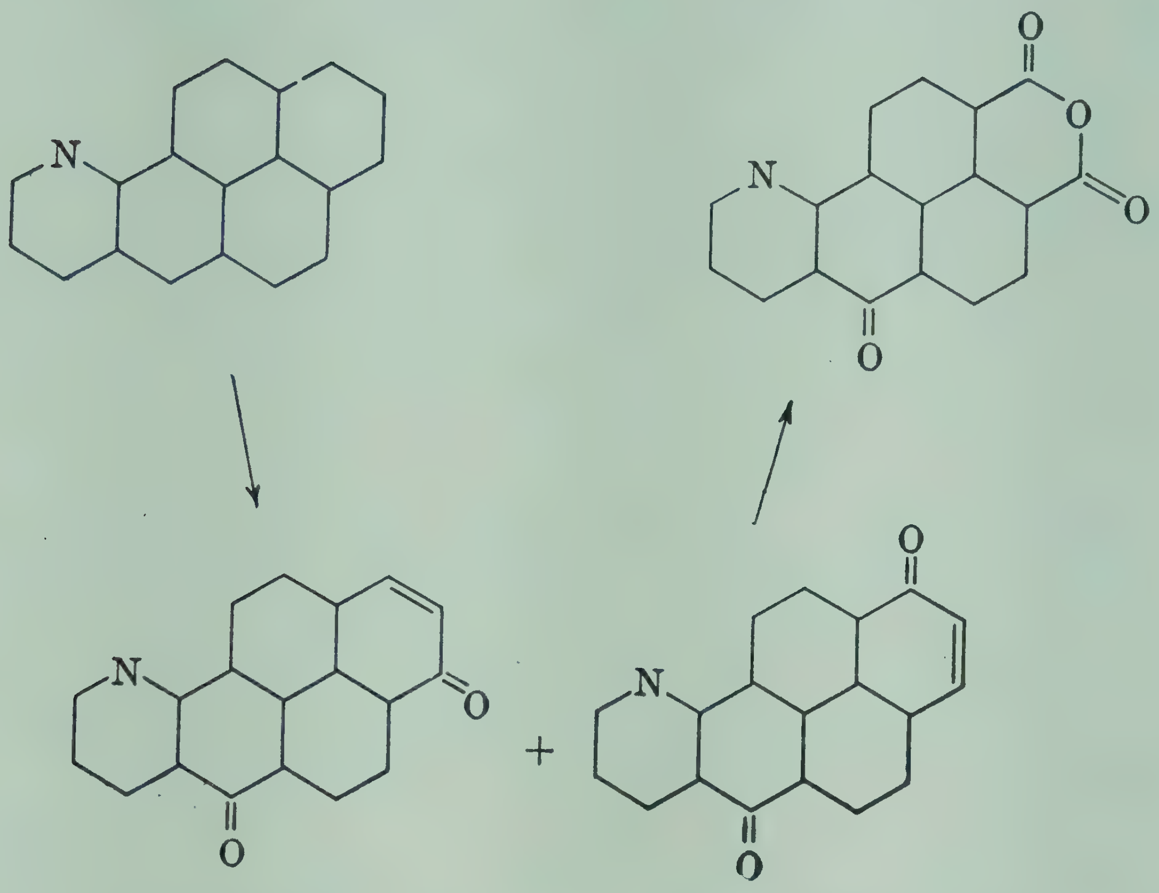
[204] IG, BP 349,059; 427,485; DRP Anm. J. 43,215; Anm. I. 50,105.



(I)



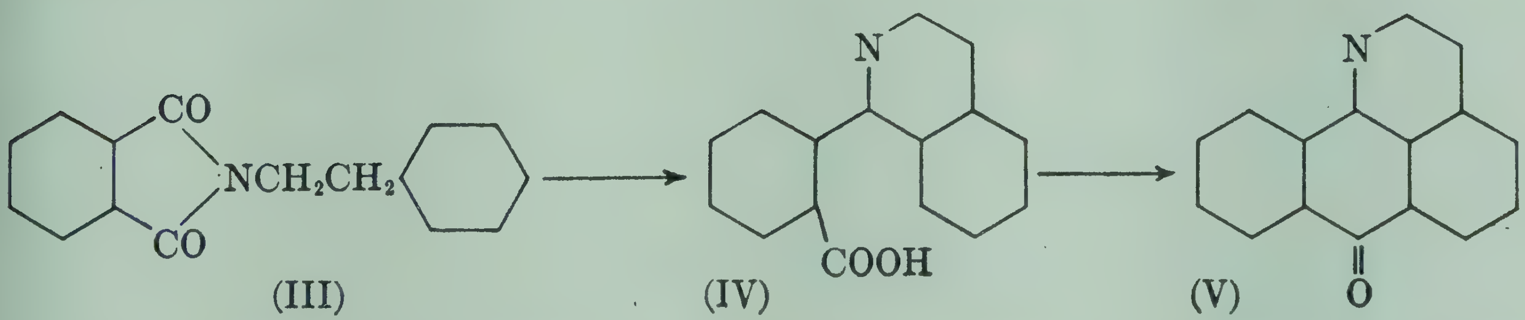
(II)



cis, orange-red

trans, yellow

The novel method[178] by which flavanthrone was synthesized from 2,2′-diaminodiphenyl has been applied to β-phenylethylphthalimide (III), which gives, via 1-*o*-carboxyphenyl*iso*quinoline (IV), 1-azabenzanthrone (V).

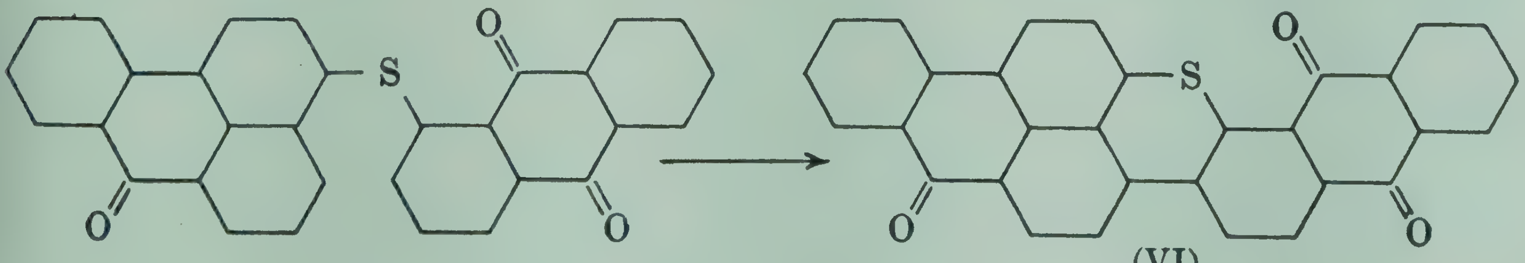


(III)

(IV)

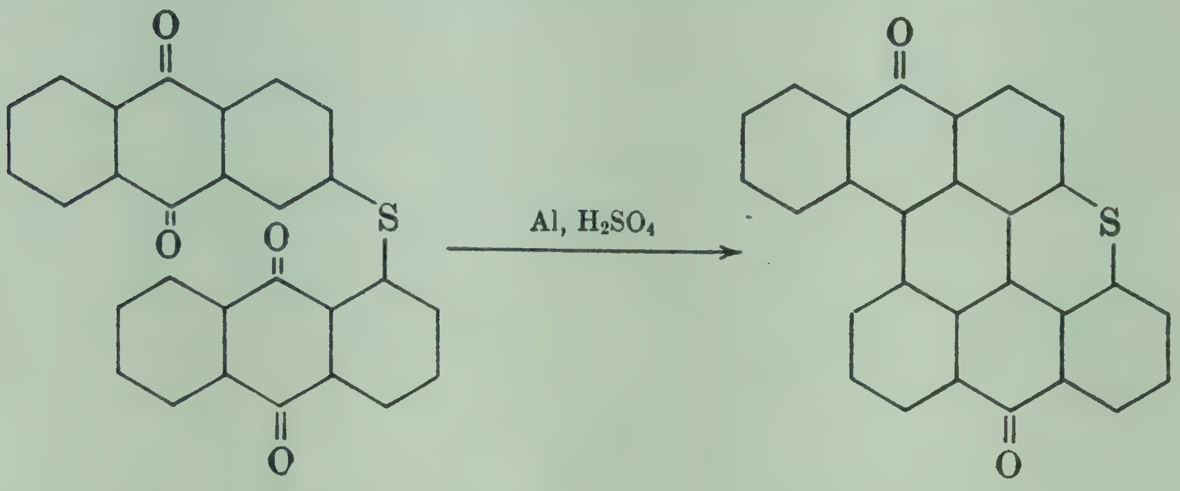
(V)

The sulfur analog (VI) of Indanthrene Olive Green B is readily obtained by heating 3-benzanthronyl 1-anthraquinonyl sulfide with

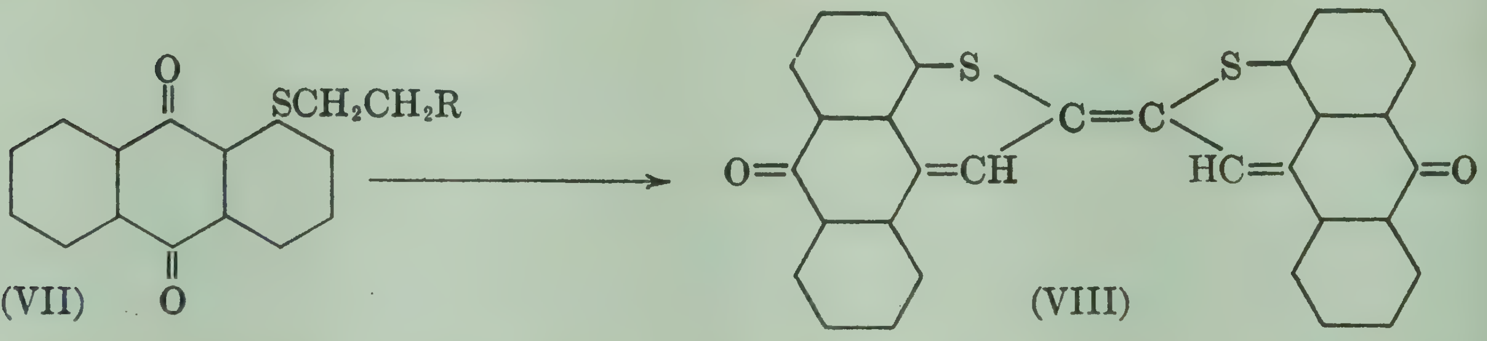


(VI)

methanolic caustic potash at about 130°, and it dyes blue-green shades of excellent fastness.[205] An interesting sulfur analog of naphthodianthrone is a very fast green dye, Vat Olive Green P409, made in the IG laboratories; its high cost prevented the addition of the dye to the selling range.[2] The dye may be purified by fractional precipitation from sulfuric acid,[206] or brightened in shade and improved in fastness by halogenation.[207] Nitration and reduction of this dye have also been described. The amines may be acylated, condensed with halogen derivatives, or converted into pyridino compounds, yielding green to gray vat dyes.[208] A new type of anthraquinone vat dye has been obtained by heating α-anthraquinonyl thioethers of the type (VII), where R is an acidic group such as carboxyl. The products (VIII) dye blue-green shades.[209]



Vat Olive Green P409



(VII) (VIII)

The fusion of two molecules of dibenzopyrenequinone to a thiophene or furan ring results in golden orange dyes.[210]

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[205] Scalera and American Cyanamid, USP 2,441,512.

[206] IG, BP 469,969.

[207] IG, BP 457,055.

[208] IG, DRP Anm. J. 55,165.

[209] IG, DRP Anm. J. 48,615.

[210] IG, DRP 741,735.

CHAPTER XXXIII

INDIGOID AND THIOINDIGOID DYES

Indigo has been known in India for many centuries, and the coloring power of the indigo plant has been mentioned in Sanskrit literature of remote antiquity. The dye was introduced into Europe from India soon after 1500 A.D., and until the early years of this century when synthetic indigo achieved commercial success in competition with the natural product, indigo was one of the major commodities in the export trade of India. The ancient Romans and Egyptians had knowledge of indigo, and in Europe the woad plant (*Isatis tinctoria*), which also yields indigo, was at one time largely cultivated.[1] There are several plants from which indigo can be isolated, but those used commercially belong to the genus *Indigofera*, grown in India, China, and other tropical and subtropical regions. The coloring matter does not occur as such in the indigo plant, but as indican, the glucoside of indoxyl. When the plant is extracted with water and the liquor is allowed to ferment, the glucoside is hydrolyzed and indoxyl is then oxidized by means of air to indigo. Natural indigo contains besides indigotin, which is the essential tinctorial constituent, varying proportions of indirubin (an isomer of indigotin formed from indoxyl by a side reaction), indigo brown (an amorphous substance of undetermined constitution, probably also derived from indoxyl), gluten, the flavonol kaempferol ("indigo yellow"), and mineral matter. The dyeing properties of natural and synthetic indigo are therefore not identical. Natural indigo has some advantages over pure indigo (indigotin), and attempts have been made from time to time to give the indigo plant a new lease of life by better methods of cultivation, selection of plant strains with high indigotin content, improved processes for the isolation of the dye, standardization of the product with a guaranteed indigotin content, and utilization of the plant residues as a nitrogenous manure.

Indigo and indigoid dyes are vat colors applicable to both cellulose and protein fibers, but more important for the latter. Indigo itself has considerably better fastness on wool than it has on cotton. Synthetic indigo appeared on the market in 1897, and notwithstanding the discovery of faster vat blues of the anthraquinone class, indigo has continued to hold its own. The importance attached to successful manufacture of synthetic indigo can be judged by the fact that BASF alone are stated as having spent a million pounds on their experiments to develop technically feasible processes. The annual pre-war consumption of indigo was estimated at 10 million pounds, a figure exceeded by not more than four or five other dyes. Research on the constitution and syntheses of indigo opened up a whole new field, and numerous analogous indigoid and thioindigoid dyes have been synthesized and made technically. Apart from indigo itself, the thioindigoids constitute a much more important series than the indigoids, finding wide application in wool dyeing and calico printing, and an extensive range of shades is available in the series. Recent research on indigoid vat dyes of practical value has been almost entirely restricted to compounds containing sulfur in both halves of the dye molecule (the true thioindigoids) or in one half; the latter type provides larger scope for synthesis, but the true thioindigoids are far more valuable as dyes. Since indigo is reddish blue, the color variations which it is possible to obtain by substitution are limited; thioindigo on the other hand is red, and a variety of shades can be produced by suitable substitution.

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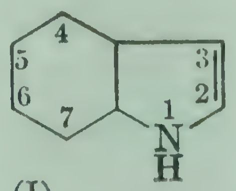
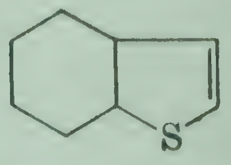
[1] For an account of natural indigo, see Perkin and Everest, The Natural Organic Colouring Matters, Longmans, London, 1918.

Synthetic indigo, in the course of its technical development, has had wider repercussions on the chemical industry as a whole than any other single dye; examples are the oxidation of naphthalene to phthalic anhydride, first by means of sulfuric acid and later by catalytic oxidation, the production of cheap chlorine by electrolysis of salt, and the preparation of formaldehyde-sulfoxylate.

Classification and nomenclature of indigoid and thioindigoid dyes. The coloring matters of this group[2–4] contain the common chromophoric chain $-CO-\underset{|}{C}=\underset{|}{C}-CO-$ and they are derived from indole (I) or thionaphthene (II). Two units are linked together to form a dye molecule; the dyes are regarded as symmetrical or unsymmetrical according as the linkage is in the 2,2′- or 2,3′-positions. In the system of nomenclature proposed by Jacobson (1906) and Friedländer (1908), indigoid and



(I)



(II)

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[2] Thorpe and Ingold, Vat Colours, Longmans, London, 1923.

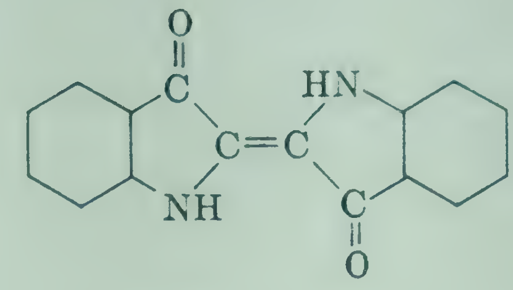
[3] Rodd in Thorpe's Dictionary of Applied Chemistry, Vol. VI, 4th ed., Longmans, London.

[4] Martinet, Matieres Colorantes des Indigoides, Bailliere, 1934.

(I) 2, 2′-Derivatives of indole and thionaphthene:

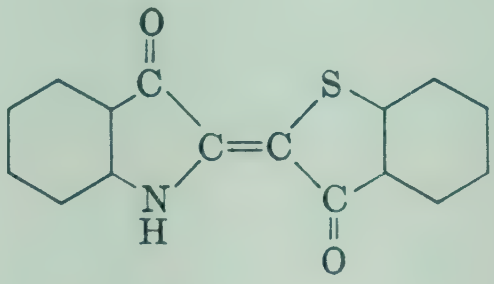
Example

(a) 2, 2′-*bis*Indoleindigos.



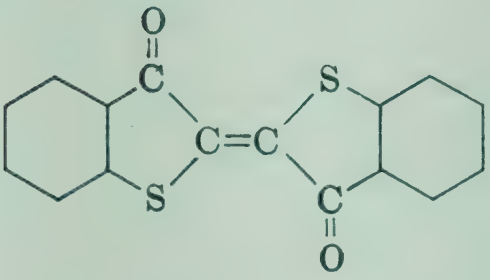
Indigo (Indigotin)

(b) 2-Indole-2′-thionaphthene-indigos.



Ciba Violet A

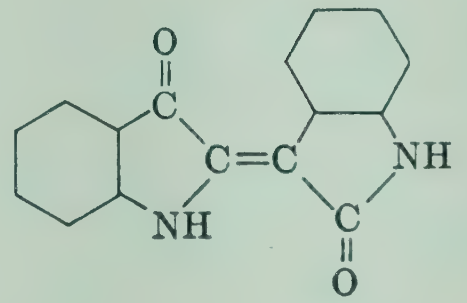
(c) 2, 2′-*bis*Thionaphthene-indigos.



Thioindigo

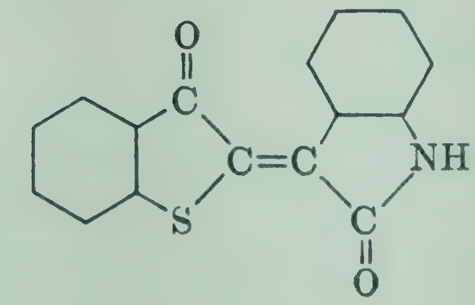
(II) 2, 3′-Derivatives of indole and thionaphthene:

(a) 2, 3′-*bis*Indole-indigos



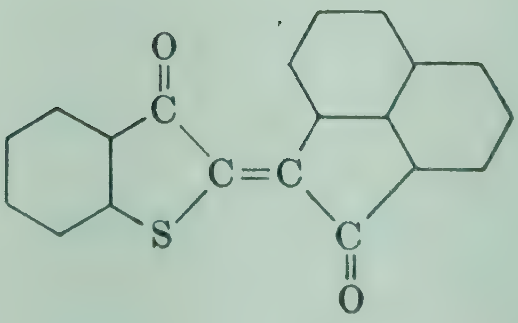
Indirubin

(b) 2-Thionaphthene-3′-indole-indigos



Thioindigo Scarlet R

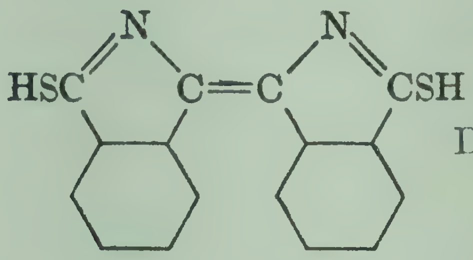
(III) Dyes in which indoxyl, thioindoxyl or isatin is condensed with a suitable component



Ciba Scarlet G

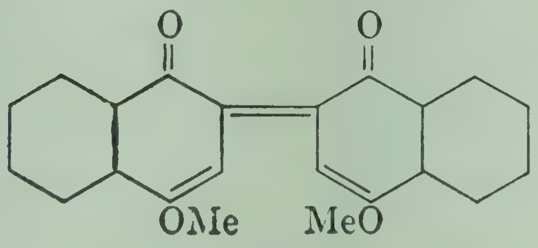
thioindigoid dyes are named by mentioning the two halves of the molecule and the points of linkage, and adding the word indigo. Thus indigo is 2,2′-bisindole-indigo; thioindigo is 2,2′-bisthionaphthene-indigo; and Thioindigo Scarlet R is 2-thionaphthene-3′-indole-indigo.

Following Bohn's classification[5] in a slightly modified form, indigoid and thioindigoid dyes may be divided into three large groups. 3,3′-Indole-indigo (*iso*indigo) and similarly constituted compounds derived from thionaphthene have been described, but they are valueless as dyes. Thus phthalonitrile is quantitatively converted by hydrogen sulfide in alcoholic ammonia to the purplish black dithio-β-isoindigo, which behaves as a tautomeric compound with the reactions of a diimine

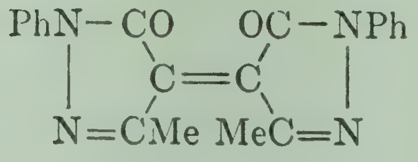


Dithio-β-isoindigo

and a dithiol and forms intensely colored compounds with metals.[6] The condensation is applicable to other *o*-dinitriles. Two other types of dyes, which are indigoid in character in the sense of their containing the $-\mathrm{CO}-\underset{|}{\mathrm{C}}=\underset{|}{\mathrm{C}}-\mathrm{CO}-$ chain, may be mentioned, although they are not derived from indole or thionaphthene. Russig[7] oxidized 4-methoxy-1-naphthol by means of ferric chloride to the blue dyestuff (III), which dyed as a vat color; the oxidation may be carried out on the fiber, and fur can be dyed in this manner in fast blue shades.[8] The second type is Pyrazole Blue which also dyes like indigo.[9]



(III)



Pyrazole Blue

Commercial names. IG have retained the name Indigo with suitable suffixes for indigotin and its halogenated derivatives. The thioindigoid dyes are grouped under different names in accordance with their dyeing and fastness properties. The few members of the series which have high all-round fastness and are useful for cotton are included in the Indanthrene range; those with lower all-round fastness are among the Algol colors; dyes particularly valuable for calico printing are specified as Indanthrene Printing colors. The Helindone range, with few exceptions such as Yellow 3GN and Brown 3GN which are anthraquinonoids, comprises indigoid and thioindigoid dyes; these are primarily wool colors, but in printing they give fast bright prints on cotton and are largely used in calico printing. However, the Helindones suitable for calico printing have now been mostly included in the Indanthrene Printing class. ICI group the indigoids and thioindigoids as Durindones; Ciba as Ciba dyes; du Pont among Sulfanthrenes; Calco among Calcosols; and NAC as Vat dyes.

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[5] *Ber.* **43,** 992 (1910).

[6] Drew and Kelly, *JCS* 625, 630, 637 (**1941**).

[7] *J. prakt. Chem.* (ii) **62,** 30 (1900).

[8] IG, BP 407,066.

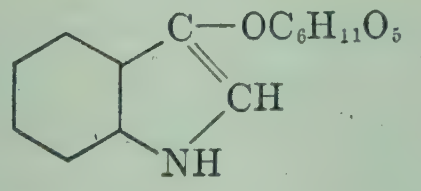
[9] Knorr, *Ann.* **238,** 137 (1887).

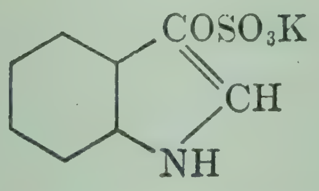
2,2′-*bis*Indole-Indigos

Indigo (CI 1177), isolated from the plant or prepared synthetically, forms a dark blue, lustrous powder. It sublimes without decomposition, and crystallizes from nitrobenzene, aniline and other high boiling organic solvents in glistening, deep blue, rhombic prisms (m.p. 390–392°, decomp.), which exhibit a coppery reflex on rubbing. A particularly good solvent for crystallizing indigo is phthalic anhydride. It is insoluble in alkalis and dilute acids. On reduction with alkaline reducing agents it forms a pale yellow solution, which possesses affinity for both cellulose and protein fibers. The leuco compound (Indigo White) is readily oxidized in solution by air to the parent dye; but Indigo White can be isolated and crystallized in colorless leaflets. The determination of the constitution of indigo, due to Baeyer, is one of the classics of organic chemistry, and the story has been told in many books. Some of the reactions on which Baeyer's constitution was based are outlined in Chart 1.

Among the degradation products of indigo, indoxyl (bright yellow prisms, m.p. 85°) is of special interest; it occurs as its glucoside, indican, in the indigo plant, and indoxyl in alkaline solution is easily and quantitatively converted into indigo by air oxidation. Syntheses of indigo therefore invariably proceed through indoxyl. The enolic character of indoxyl, which reacts in two tautomeric forms, is shown by its ready solubility in aqueous alkali and the red color it gives with ferric chloride in alcoholic solution. "Urine indican," isolated from the urine of mammals, is potassium indoxyl sulfate, and it results from the putrefac-

Indican

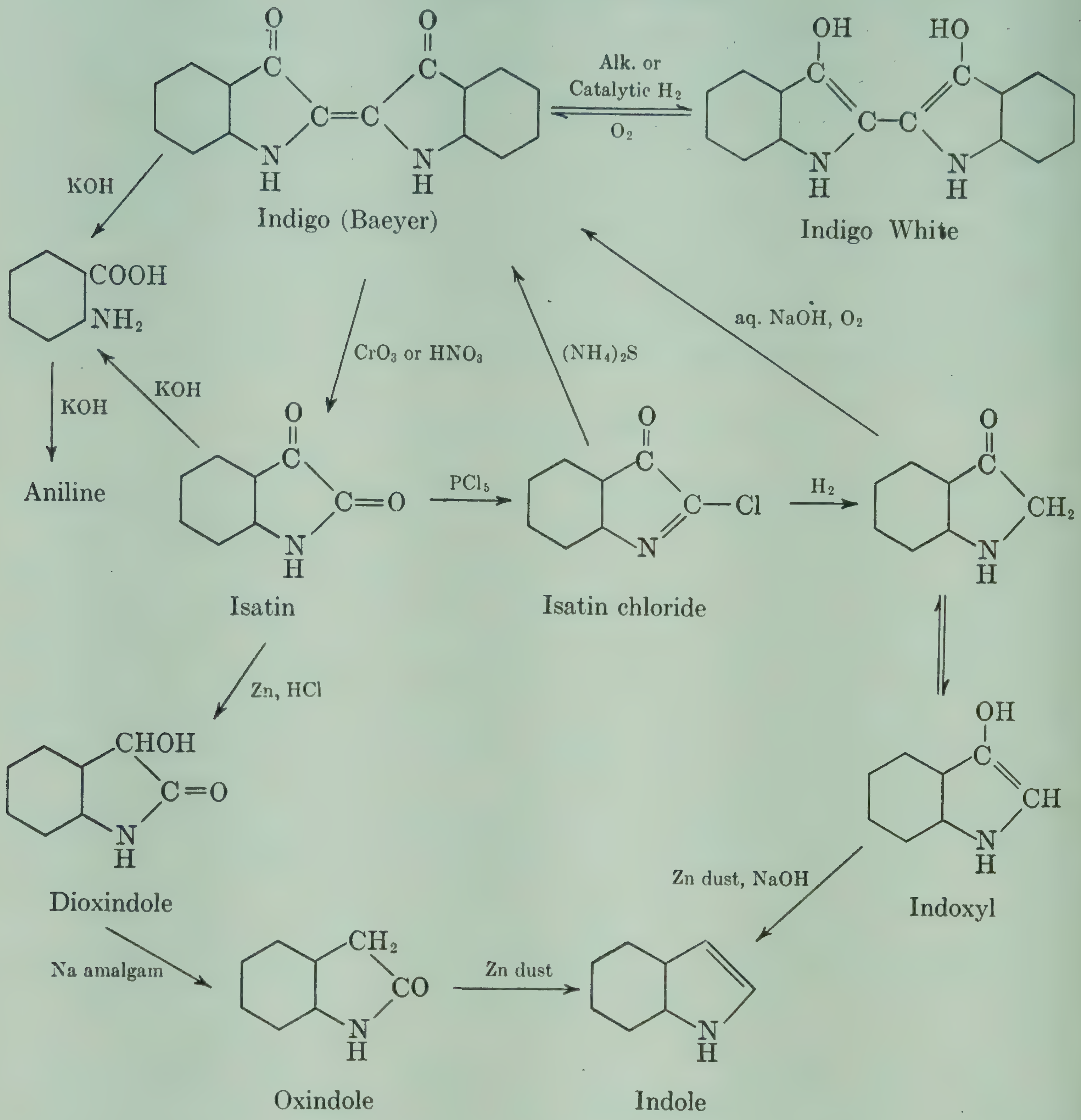




Urine indican

CHART 1

Constitution of Indigo


O
O
C
C
C=C
N
H
N
H
Indigo (Baeyer)
Alk. or
Catalytic H₂
O₂
OH
HO
C
C
C—C
N
H
N
H
Indigo White
KOH
COOH
NH₂
KOH
Aniline
KOH
CrO₃ or HNO₃
(NH₄)₂S
aq. NaOH, O₂
O
C
C=O
N
H
Isatin
PCl₅
O
C
C—Cl
N
Isatin chloride
H₂
O
C
CH₂
N
H
Zn, HCl
CHOH
C=O
N
H
Dioxindole
OH
C
CH
N
H
Indoxyl
Zn dust, NaOH
Na amalgam
CH₂
CO
N
H
Oxindole
Zn dust
N
H
Indole

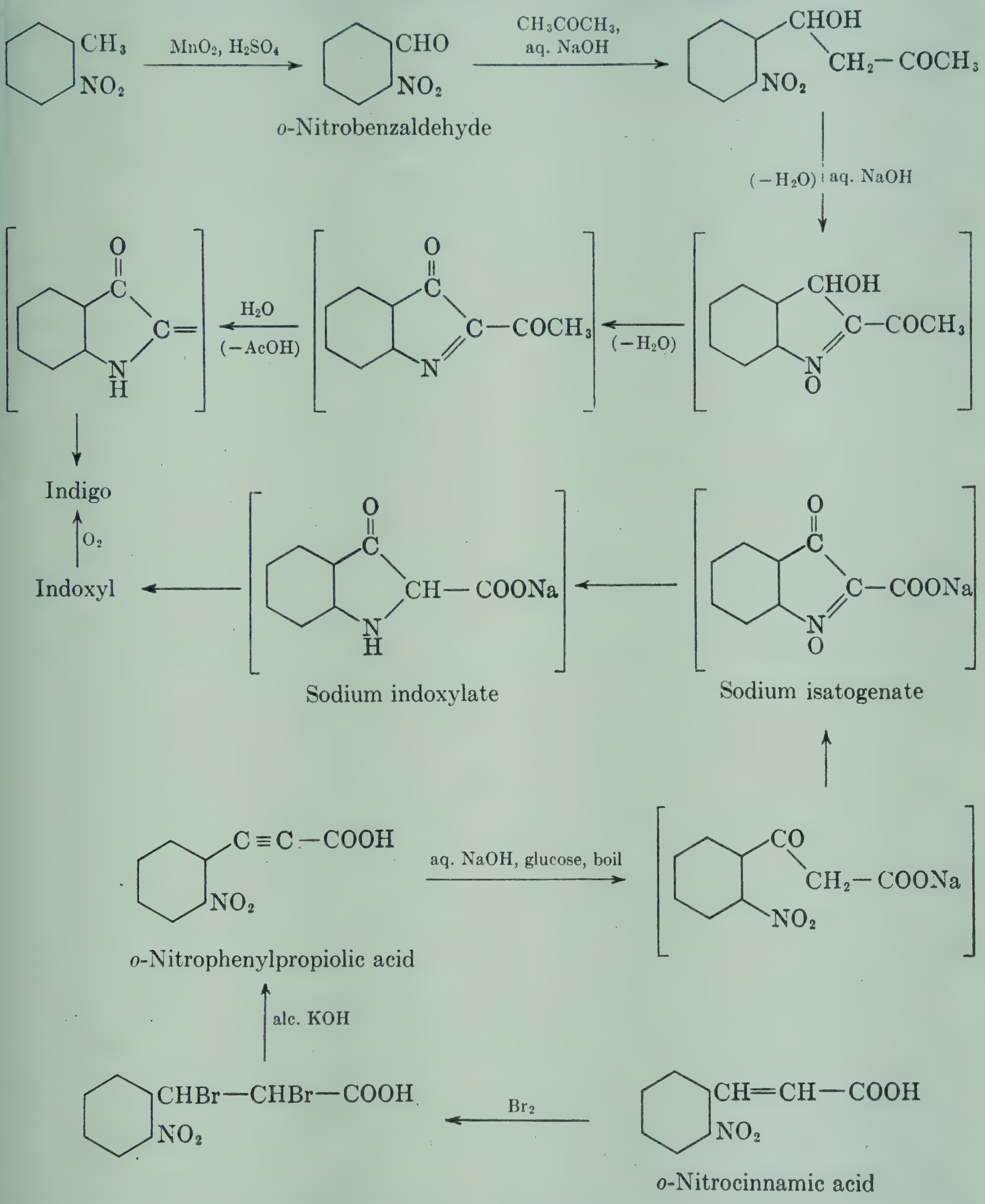
tive formation of indole from tryptophane; indole oxidizes to indoxyl in the liver, and indoxyl conjugates with sulfuric acid. Urine indican is estimated by oxidation to indigo with ferric chloride.

Engler and Emmerling (1870) prepared indigo synthetically in minute quantities by distilling *o*-nitroacetophenone with zinc dust and soda-lime, and Nencki (1875) by the oxidation of indole. Baeyer achieved several syntheses of indigo (e.g., by the reduction of isatin chloride) prior to his complete elucidation of its structure in 1883. The first real synthesis (1880) started with *o*-nitrocinnamic acid, converted via the dibromide into *o*-nitrophenylpropiolic acid, which gave indigo by alkaline reduction. The second method (Chart 2), still of interest

CHART 2

BAEYER'S SYNTHESES OF INDIGO

FROM *o*-NITROBENZALDEHYDE AND *o*-NITROCINNAMIC ACID


CH3
NO2
MnO2, H2SO4
CHO
NO2
o-Nitrobenzaldehyde
CH3COCH3, aq. NaOH
CHOH
CH2—COCH3
NO2
(−H2O) aq. NaOH
CHOH
C—COCH3
N
O
(−H2O)
O
C
C—COCH3
N
H2O (−AcOH)
O
C
C=
N
H
Indigo
O2
Indoxyl
O
C
CH—COONa
N
H
Sodium indoxylate
O
C
C—COONa
N
O
Sodium isatogenate
C≡C—COOH
NO2
o-Nitrophenylpropiolic acid
aq. NaOH, glucose, boil
CO
CH2—COONa
NO2
alc. KOH
CHBr—CHBr—COOH
NO2
Br2
CH=CH—COOH
NO2
o-Nitrocinnamic acid

as a test for *o*-nitroaldehydes,[10] was used for a short time in industry. Over thirty syntheses have since been developed, of which however only two are used in technical practice.

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[10] For a study of the mechanism of this reaction and the influence of substituents, see Tanasescu and Georgescu, *Bull. soc. chim.* **51,** 234 (1932); Hinkel, Ayling, and Morgan, *JCS* 985 (**1932**).

The Baeyer formula for indigo is firmly based on degradative and synthetical evidence. The conjugated system, resembling the *p*-quinones, accounts for the behavior of both the indigoids and suitably substituted anthraquinone derivatives as vat dyes, which undergo reduction to an alkali-soluble leuco compound and ready reoxidation. However, further elaboration of the classical formula is required for explaining some of the properties of indigo, such as its high melting point, stability, the purple-red color in the vapor phase and in nonpolar solvents (e.g. paraffin), and the blue color in polar solvents (e.g. aniline or phenol) in which it gives values for the molecular weight twice the calculated figure. Indigo has been shown[11] by X-ray spectrography to have the *trans* configuration (I); two stereoisomers of indigo have been identified, but the *cis* form reverts spontaneously to the *trans* isomer in a few hours even in the solid state.[12] Indigo reacts with oxalyl chloride in boiling nitrobenzene (and also at room temperature) to form oxalylindigo, which must be derived from *cis*-indigo. Indigo freshly prepared by oxidation of the vat is more soluble in solvents such as dioxane, and is therefore the *cis* form.[13] Robinson has indicated a structural analogy between *trans*-indigo and Indanthrene Blue.[14] Kuhn has associated the tetrapolar structure (IA) with the *trans* configuration and the color; the aggregates in polar solvents are formed by two molecules oriented alongside each other by the attraction of the opposite charges.[15] Hydrogen bonding between the nitrogen and oxygen atoms in (IB) would explain the stability of indigo and the resistance of the keto and imino groups to their characteristic reactions. With magnesium methyl iodide, however, two molecules of methane are evolved, showing the presence of two active hydrogen atoms.[16] The properties of the indigo molecule are best explained by regarding it as a resonance hybrid of structures such as (I), (IB), (IC) and (ID).[17] The quadrupolar structure (IA) must be less important.

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[11] Reis and Schneider, *Z. Krist.* **68,** 543 (1928).

[12] Heller, *Ber.* **72,** 1858 (1939).

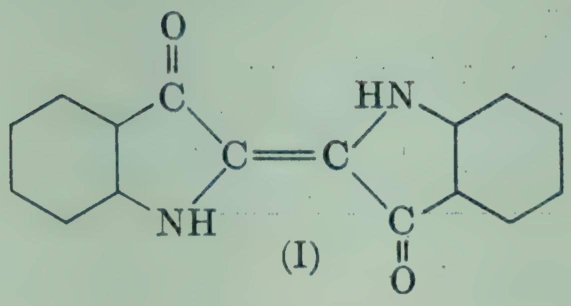
[13] Friedländer and Sander, *Ber.* **57,** 648 (1924); van Alphen, *ibid.* **72,** 525 (1939).

[14] *J. Soc. Dyers Colourists* **37,** 77 (1921).

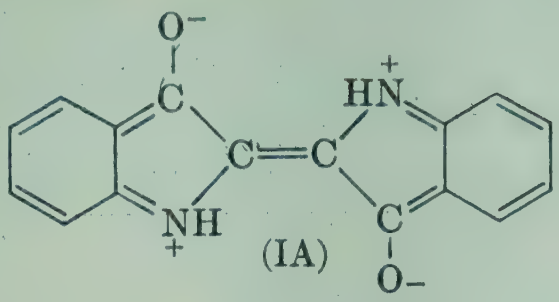
[15] Kuhn, *Naturwissenschaften* **20,** 618 (1932).

[16] Kuhn and Machemer, *Ber.* **61,** 118 (1928).

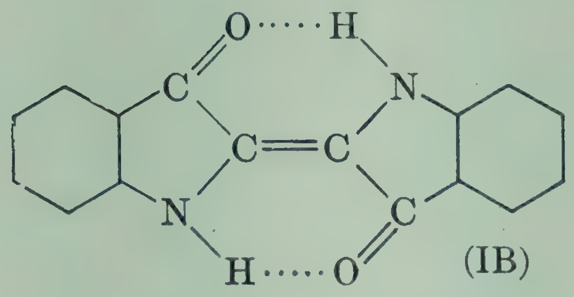
[17] Cf. van Alphen, *Rec. trav. chim.* **57,** 911 (1938). See also Knott, *J. Soc. Dyers Colourists* **67,** 302 (1951).



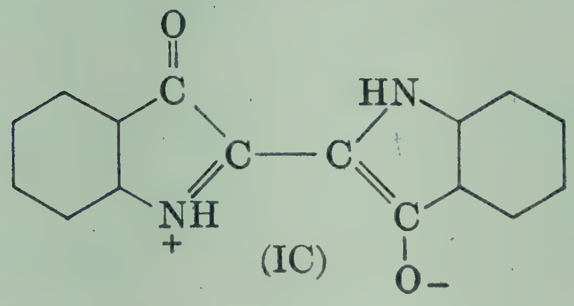
(I)



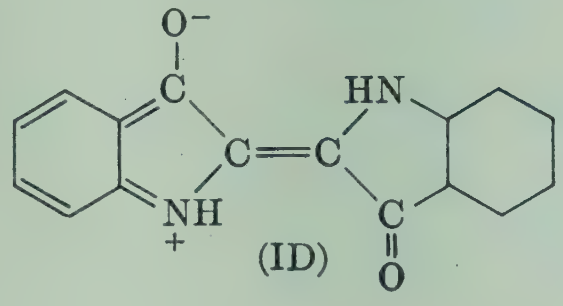
(IA)



(IB)



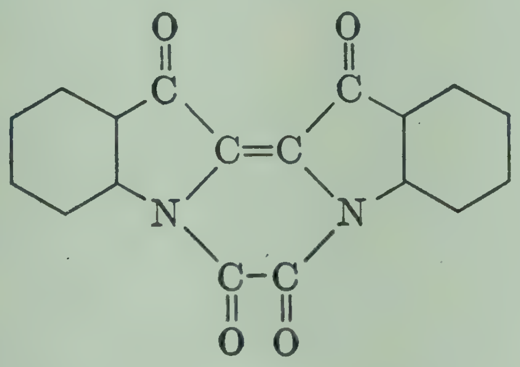
(IC)

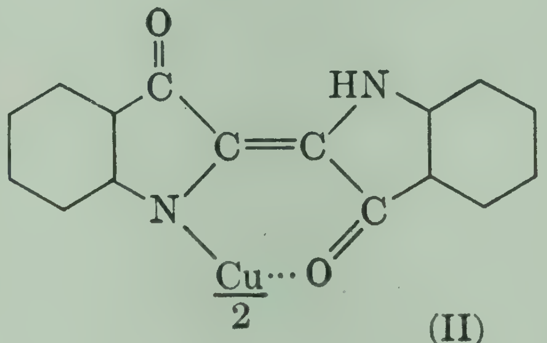


(ID)

Indigo forms metallic derivatives which are of interest in relation to the metal phthalocyanines. Kunz has prepared the copper and iron derivatives.[18] The iron compound exhibits a remarkable similarity to hemoglobin, absorbing one molecule of oxygen for each atom of iron, and releasing it in a vacuum. Kuhn and Machemer have shown that copper-indigo has the structure (II), in which one copper atom is in combination with a nitrogen atom and a carbonyl oxygen of each of two molecules of indigo in the *trans* configuration.[16]

Oxalylindigo





(II)

Posner has determined the absorption spectra of indigo, a series of its substitution products, and Thioindigo Red (Table I).[19] All substituents, including those which produce a bathochromic shift in the wave length of maximum absorption, have a marked hypochromic effect. Thioindigo absorbs at lower wave length than indigo, but the intensity of the absorption is the same for the two dyes.

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[18] *Ber.* **55,** 3688 (1922).

[19] *Ber.* **59,** 1799 (1926).

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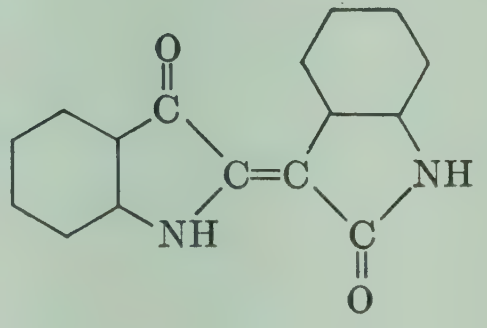
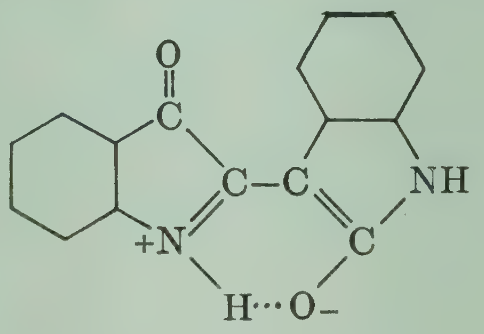
TABLE I
ABSORPTION MAXIMA OF INDIGO AND ITS DERIVATIVES

Substance	λ*max. A*	*Relative intensity*
Indigo	5910	1.00
N,*N*′-Diethylindigo	6520	0.31
N,*N*′-Dibenzoylindigo	5750	0.31
N,*N*′-Diacetylindigo	5450	0.35
7,7′-Dimethylindigo	6040	0.54
N-Benzoyl-7,7′-dimethylindigo	5750	0.31
Indigo phenylacetic ester	5550	0.31
Indigo malonic ester	5500	0.31
Thioindigo	5400	1.00

There is a hypsochromic shift in passing from indigo (blue) to indirubin (violet red), which is explicable when the resonance of the polar structures is considered (cf. IIIA, B and C). In structures (IIIB) and (IIIC), as in structure (ID) for indigo, a benzene ring is *o*-quinonoid, so that the contributions made by these structures can only be at the expense of the benzenoid resonance. While a second structure equivalent to (IC), involving the polarization of the other CO and NH groups, can be written for indigo, only one structure (IIIA) of this type is possible for indirubin (IIIA and IIIB not being equivalent). As a result, the excited state for indirubin represents higher energy in comparison with indigo, and indirubin absorbs at shorter wave length. These suggestions find further support when the brownish red color of isoindigo is considered. Resonance structures such as (IV) can lead to deep color, but there are two unfavorable factors. The contribution made by (IV) must be at the expense of the benzenoid resonance of a benzene ring; and because

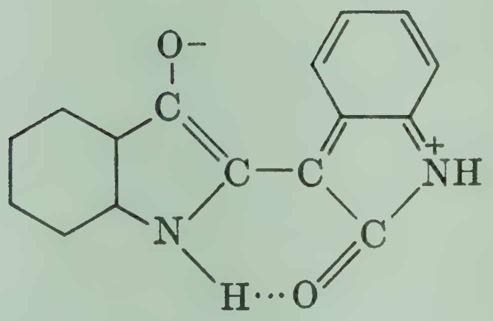
Indirubin
(III)

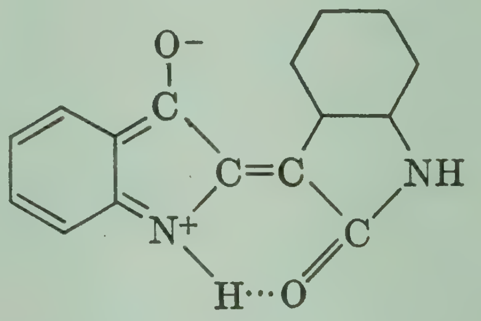




(IIIA)

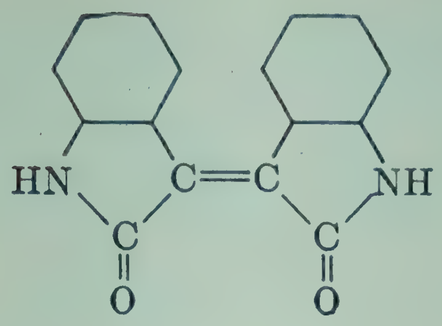
(IIIB)

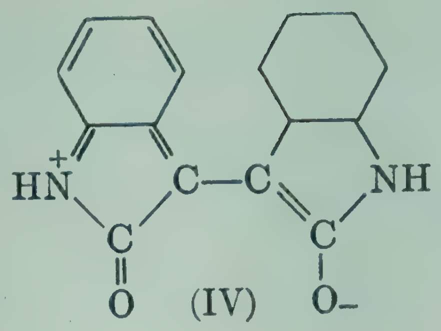




(IIIC)

Isoindigo





(IV)

of the contiguity of the keto and imino groups in each half of the molecule, this resonance must also be at the expense of the amide resonance. Thus there is a marked decrease in absorption in comparison with indigo and indirubin.

Technical syntheses of indigo.[20] The two methods discovered by Heumann in 1890, consisting in the caustic potash fusion of the alkali salt of phenylglycine (I) or its *o*-carboxylic acid (II) to form indoxyl which undergoes quantitative oxidation in alkaline solution to indigo have been used until recently. There have naturally been many improvements in the chemical and chemical engineering aspects of the processes. Methods for the preparation of (I) and (II) are illustrated in Chart 3. The phenylglycine *o*-carboxylic acid method, which gave a better yield, received greater attention from BASF, who adopted the process and marketed synthetic indigo in 1897. Yields as high as 89% can be obtained by fusing (II) with 12–16 moles of potassium hydroxide at 260° for 10 minutes.[21] It was later found by Pfleger (1901) that equally good results could be obtained from the cheaper phenylglycine, if sodamide is used for the fusion, when the reaction proceeds very smoothly and in nearly quantitative yield; and indigo (MLB) was manufactured in this manner.[22] A relatively low temperature (about 200°) is sufficient because of the low m.p. (155°) of sodamide. Hazards in handling sodamide can be avoided by using metallic sodium and passing dry ammonia into the reaction mixture.[20] A mixture of caustic potash, caustic soda and sodamide is usually employed for the fusion of sodium phenylglycinate. The sodamide process is also applicable to phenylglycine *o*-carboxylic acid. While the great increase in the production of benzene by the general introduction of by-product coke-ovens has favored the success of the phenylglycine process, the *o*-carboxylic acid route found a stimulus in the cheap production of phthalic anhydride by the catalytic oxidation of naphthalene in the vapor phase. However, the phthalic anhydride route to indigo has now completely lost its commercial importance.

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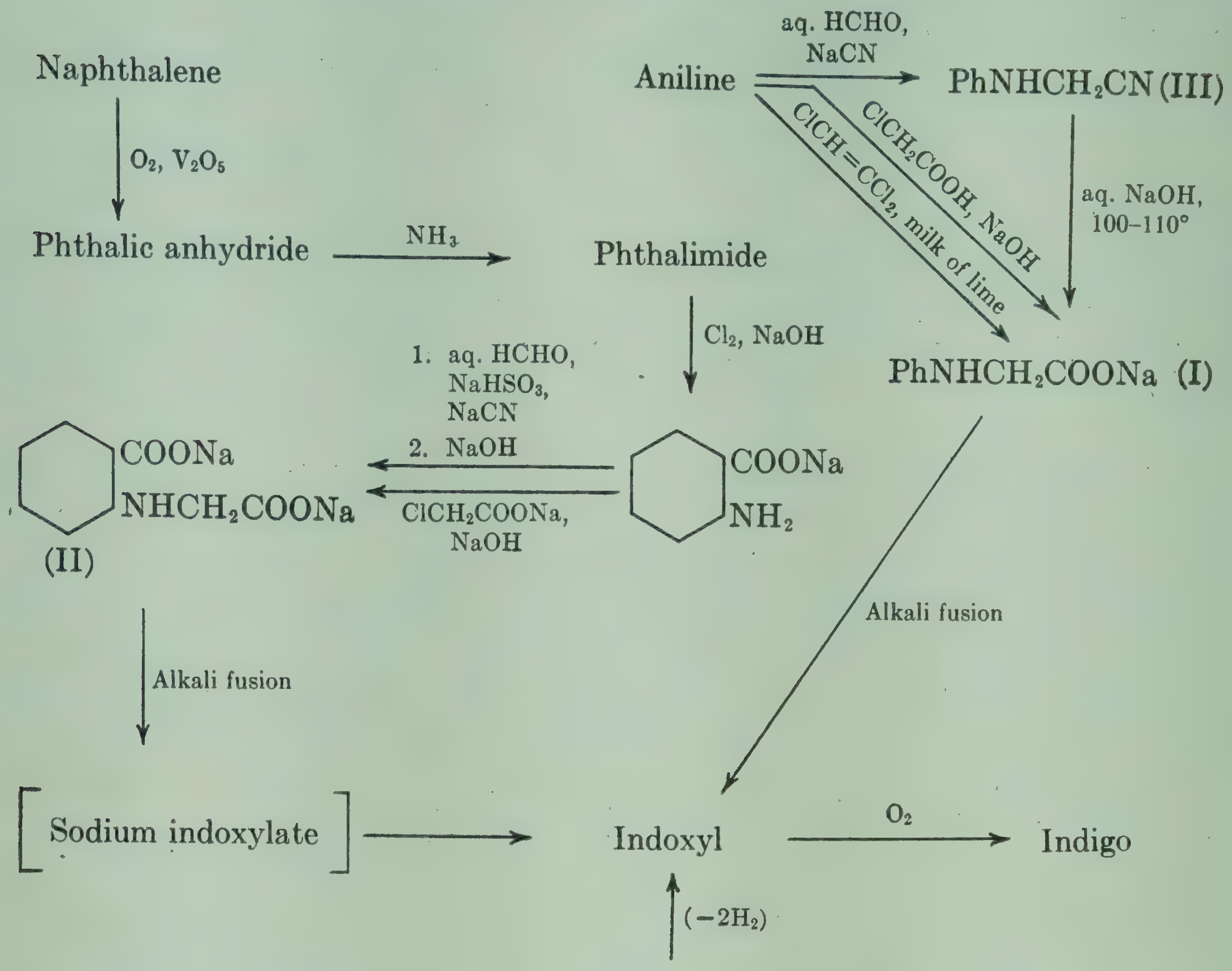
[20] Henesey, *J. Soc. Dyers Colourists* **54,** 105 (1938). See also Holzach, *Angew. Chem.* **60A,** 200 (1948).

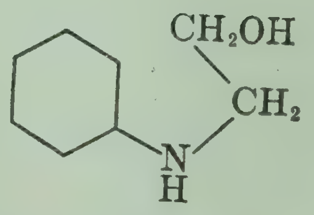
[21] Phillips, *Ind. Eng. Chem.* **13,** 759 (1921).

[22] Gold- and Silber-scheide-Anst., DRP 137,955; 141,749; 180,394.

CHART 3

Syntheses of Indoxyl and Indigo


Naphthalene
O₂, V₂O₅
Phthalic anhydride
NH₃
Phthalimide
Cl₂, NaOH
Aniline
aq. HCHO, NaCN
PhNHCH₂CN (III)
ClCH₂COOH, NaOH
ClCH=CCl₂, milk of lime
aq. NaOH, 100–110°
PhNHCH₂COONa (I)
COONa
NHCH₂COONa
(II)
1. aq. HCHO, NaHSO₃, NaCN
2. NaOH
ClCH₂COONa, NaOH
COONa
NH₂
Alkali fusion
Alkali fusion
Sodium indoxylate
Indoxyl
O₂
Indigo
(−2H₂)


CH₂OH
CH₂
N
H

(IV)

In the IG Ludwigshafen process for phenylglycine,[23] aniline (4650 kg.), 30% formaldehyde (2500) and water (2500) in an autoclave, under a carbon dioxide pressure of 3 atms., are treated with a 30% solution (3600 l.) of sodium cyanide at about 50°, and the mixture then heated to 90° for 30 minutes. On adding cold water (3500) and transferring to a separator, the upper layer of the nitrile (III) and aniline are separated and heated at 110° in an autoclave with caustic potash (735), caustic soda (525) and water (15000) for 1½ hours. Ammonia is then released at 100° during 3½ hours, and from the condensate aniline is recovered. The alkali phenylglycinate solution, which contains some unconverted aniline, is cooled, separated from the bicarbonate, and extracted with hot benzene by a counter-current process in a series of towers. The aniline-free glycine solution is treated with carbon dioxide until weakly alkaline to phenolphthalein, screened to remove sodium carbonate, evaporated to about 55% in a vacuum evaporator, and finally dried down on a vacuum double drum dryer. This potassium-sodium salt of phenylglycine is fused with sodamide and caustic alkali at 220° for 5–6 hours under pressure in the inert atmosphere provided by the liberated ammonia.[20] The mixed alkali (KOH:NaOH as 2:1) is about 4 times the weight of the glycine, and according to Henesey the best yield is obtained by using 2 moles sodamide for one of the glycine.[20] Fierz-David describes somewhat different conditions of alkali proportions and temperature. The fusion mass is finally discharged into ice and water, and indoxyl oxidized to indigo by blowing in air, and the press cake slurried with water, acidified, refiltered, washed and finally standardized. An overall yield of 90% has been claimed, when the recoveries are taken into account.[20] During the fusion, about 8% of the phenylglycine undergoes decarboxylation to monomethylaniline which partly breaks down further to aniline; during the oxidation some anthranilic acid is formed, and all these three by-products are recoverable. Another by-product is quindoline-11-carboxylic acid (Flavindine), formed by the condensation of indoxyl with isatinic acid.[24] An important factor in the economy of indigo manufacture is the recovery of caustic alkali.

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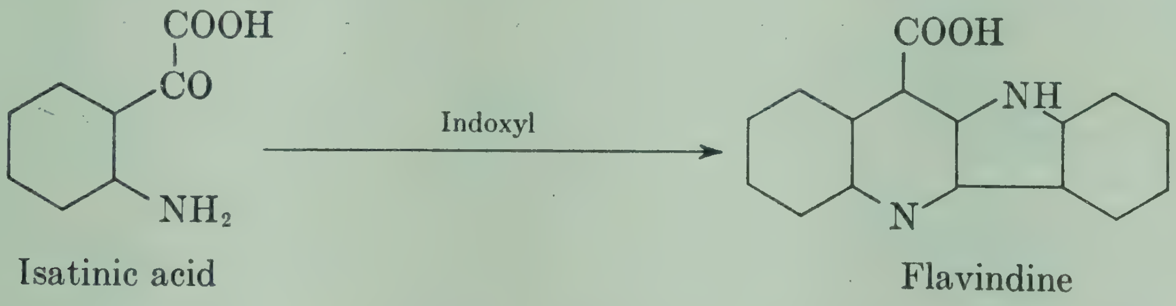
[23] *BIOS* **986**.



Between 1912 and 1914 BASF manufactured large quantities of indigo by a third method, the fusion of β-hydroxyethylaniline (IV), obtained from aniline and ethylene chlorohydrin, with caustic alkali and quicklime; indoxyl is formed with evolution of hydrogen.[20] For many years synthetic indigo was a German monopoly, but after the first world war Great Britain and the United States stepped into the field. As a result the price of indigo went down ultimately to less than a dollar per pound on a 100% basis, and IG proceeded to develop continuous processes for indigo manufacture with the object of lowering the cost of production. Two processes worked out by IG at Ludwigshafen and Hoechst have been described by Kern and Stenerson.[25] In the Ludwigshafen process, which was operated on a plant scale, aniline, 30% formaldehyde and 100% hydrocyanic acid were condensed at 96° to form (III); this was hydrolyzed in two steps: at 60° to the amide and at 103° to sodium phenylglycinate. Benzene extraction and the production of the solid glycinate (yield 94%) were carried out as already described. For the fusion to sodium indoxyl, sodamide and a molal mixture of potassium sodium hydroxide at 216° were used. In the Hoechst method, which did not go beyond the pilot plant stage, β-hydroxyethylaniline (IV) was made by condensing aniline (8 moles) with ethylene oxide (1) at 90°; (IV) and aniline were separated by fractional distillation, and (IV) was converted into the disodium salt ($Ph{-}NHNa{-}CH_2CH_2ONa$) in two steps: the monosodium salt by heating with potassium sodium hydroxide at 200° and the di-salt by adding sodamide at the same temperature. The di-salt was heated rapidly to 300° for dehydrogenation and cooled to 235° for completing the cyclization to sodium indoxyl. An essential difference between the Ludwigshafen and Hoechst processes was that the latter required only one atom of metallic sodium as against two for the former. Although yields of 80–90% were claimed, the processes required complicated equipment and critical operation, and apparently could not compete with the batch process using phenylglycine.

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[24] Noelting and Steuer, *Ber.* **43,** 3512 (1910).

[25] *Chem. Eng. News* **24,** 3164 (1946).

Indigo is marketed as grains (60%) and paste (20%), and leucoindigo in forms suitable for wool dyeing and cotton dyeing.

Analysis of indigo. Numerous methods have been proposed, since the problem of estimating indigo, particularly in natural indigo with its complex constituents, presents many difficulties.[3, 26] Several methods, such as extraction with a solvent (aniline, phenol, nitrobenzene) or sublimation have become obsolete, and the main general method now in use is to tetrasulphonate indigo and titrate the product with an oxidizing or reducing agent. The chief oxidizing agents, among many that have been suggested from time to time, are permanganate and ceric sulfate; stoichiometrically related quantities are not consumed and the determination is empirical. Further, special treatments are necessary for eliminating errors due to the action of the oxidizing agents on the other constituents. Among reducing agents, the most convenient to use is titanous chloride.[27] Sodium formaldehyde-sulfoxylate has also been used.[28] The estimation of synthetic indigo is relatively simple, since the impurities of natural indigo are absent. An electrometric method for determining indigo, especially in reduced indigo preparations, has been described.[29]

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[26] For details of the analysis of indigo in substance and on the fiber, see Green, The Analysis of Dyestuffs, 3rd ed., Griffin, London, 1941.

[27] Knecht and Hibbert, New Reduction Methods in Volumetric Analysis, 2nd ed., Longmans, London, 1925.

[28] Jones and Spaans, *Ind. Eng. Chem.* **8,** 1001 (1916).

[29] Strafford and Stubbings, *J. Soc. Chem. Ind.* **57,** 368 (1938).

A colorimetric procedure is to oxidize the vat by hydrogen peroxide in presence of sodium protalbinate, when a blue colloidal solution is obtained which may be compared with a standard solution of indigo or a dyestuff of similar shade such as Sirius Blue B.[30]

DERIVATIVES OF INDIGO

Indigo White (CI 1178). The use of indigo in dyeing and printing has been facilitated by making it available in reduced condition, so that the vatting process is cut out. Several reduction products of indigo have been described, of which one, Indigo White, is technically important. After reduction of indigo with alkali and hydrosulfite, zinc or glucose, Indigo White may be precipitated by carbon dioxide or mineral acid. Being a dibasic acid, leucoindigo forms mono- and disodium salts; the acid salt is more stable and it is therefore preferable to prepare concentrates of the acid salt. IG employ catalytic reduction in aqueous caustic soda with hydrogen in presence of nickel. Indigo production at Hoechst was 400 tons per month of which half was sold as Indigo White. The catalyst was prepared by reduction of nickel carbonate mounted on Fuller's earth. Indigo reduction was carried out in a horizontal boiler, jacketed for steam, using 20% indigo paste, caustic soda, the catalyst and hydrogen. The leuco solution was siphoned off from the catalyst, and the procedure then varied according as whether the product was to be marketed in the form of paste or grains. For paste the leuco compound was precipitated from solution by carbon dioxide and filtered off. It was then mixed with molasses and evaporated at 50° *in vacuo* to 50% Indigo White content and dried finally in a vacuum tray dryer. For grains the leuco solution containing about 17% of Indigo White was mixed with molasses, concentrated and dried. The addition of molasses was adjusted so as to obtain grains of 50–60–70–80% indigo content.[31]

Another method of preparing Indigo White is to condense indigo (1 mole) with indoxyl (2 moles): $C_{16}H_{10}O_2N_2 + 2C_8H_7ON \rightarrow 2C_{16}H_{12}O_2N_2$. A further simplification of this procedure is to convert the indoxyl melt from phenylglycine directly into Indigo White.[32]

Leucoindigo can be acylated with acid chlorides and can be converted into ethers by means of alkyl or aralkyl chlorides. If the reagents contain a sulfonic or other solubilizing group, the dye is then made water-soluble. This has found practical application in textile printing in discharge styles. A white effect on indigo-dyed ground can be produced by printing with a mixture of a reducing agent and a quaternary ammonium salt, Leucotrope W (IG), a disulfonic acid of phenylbenzyldimethylammonium chloride. The dye in the printed portions then becomes removable by washing, since it is now soluble.

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[30] Lotichius, *J. Soc. Dyers Colourists* **55,** 87 (1939).

[31] *BIOS* **1363.**

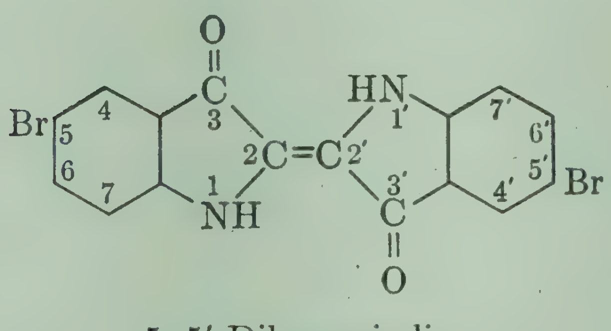
[32] Davidson, Lumsden, and ICI, BP 417,862.

Indigo and the halogenated indigos are important in the form of the Indigosols or soluble sodium salts of the sulfuric esters of the leuco compounds.[33]

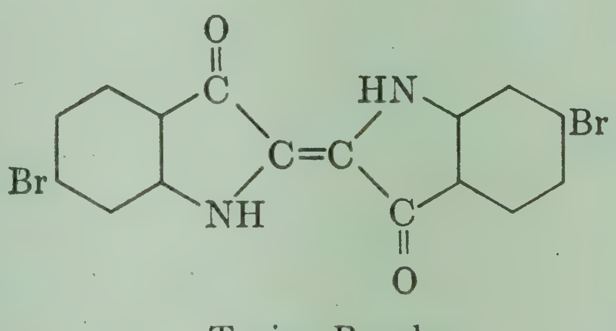
Indigo disulfonic acid. Indigo is readily sulfonated; e.g. with monohydrate or concentrated sulfuric acid at a higher temperature, Indigo Carmine (Indigo Extract; CI 1180), the 5,5′-disulfonic acid, is formed. The sodium salt is a bright blue and rather fugitive acid dye, which has now been superseded by the Patent Blues. Sulfonation of indigo is useful for bringing it into solution and estimating it by titration with permanganate.

Halogenated derivatives of indigo are important, since they are faster than indigo, particularly to chlorine, and have greater affinity for fibers.[33a] Although it has been known for a long time that indigo can be chlorinated and brominated, the technical value of the halogenation of indigo and other vat dyes was only realized when practicable methods of introducing chlorine and bromine atoms into these complex and difficultly soluble compounds became available. Engi (1907) devised bromination in nitrobenzene solution,[34] and other halogenation procedures (e.g. in concentrated sulfuric acid solution) have since been developed.

The position of the halogen atoms in indigo has a profound influence on the color. When they are *para* to the NH group (5,5′-positions), the shade is brighter and a somewhat greener blue; substitution in the 4,4′- and 7,7′-positions also gives greener shades, as in Brilliant Indigo 4G. When the halogen atoms are *para* to the CO group (6,6′-positions), the color is purple to amethyst. Substitution in the 6,6′-positions cannot be effected by direct halogenation of indigo, and such derivatives can



5, 5′-Dibromoindigo



Tyrian Purple

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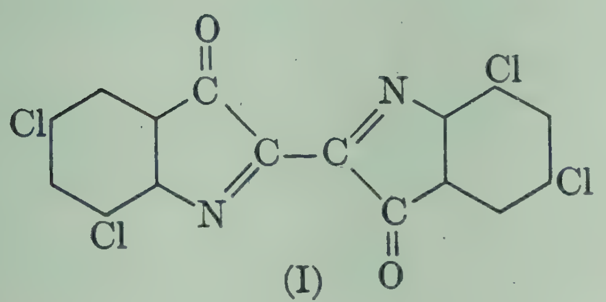
[33] See Chapter XXXIV.

[33a] The synthesis of 5,5′- and 7,7′-difluoroindigo has been reported recently; Roe and Teague, *JACS* **71,** 4019 (1949).

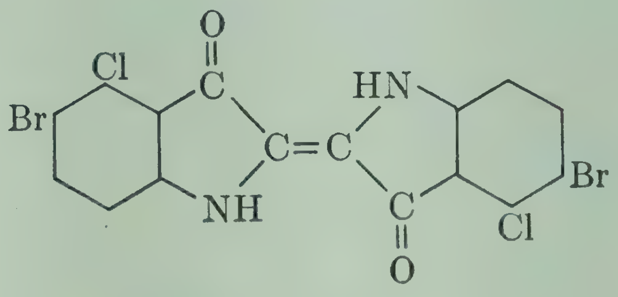
[34] Engi and Ciba, BP 5122; USP 856,687; 856,776.

only be obtained by synthesis, starting with the relevant intermediates. 6,6′-Dibromoindigo is of historical interest, since Friedländer[35] has demonstrated its identity with the purple of the ancients (Tyrian Purple), the tinctorial constituent of the glandular secretions of the mollusc, *Murex brandaris*, found on the Mediterranean coast. From 12000 molluscs Friedländer was able to isolate 1.4 g. of the dye.

The chloro and chloro-bromo derivatives of indigo, which give brighter shades than the parent dye, are marketed as Brilliant Indigos (BASF). The 5,7,5′,7′-tetrachloro (or mixed tri- and tetrachloro) derivative (I) of dehydroindigo can be prepared by chlorination in glacial acetic acid in presence of acetic anhydride and sodium acetate; subsequent treatment with aqueous caustic soda and hydrosulfite at 85° and air oxidation of the vat gives the chlorinated indigo.[36, 37] This is marketed as Brilliant Indigo B (CI 1190), at one time largely used for dyeing cotton, wool and silk and for calico printing. Brilliant Indigo 4G (CI 1189) is 4,4′-dichloro-5,5′-dibromoindigo; the dichloro indigo is prepared synthetically and then brominated.[37, 38] 2-Chloro-6-nitrobenzaldehyde (200 kg.) and acetone (400), cooled to −5°, are treated with 1% caustic soda solution (1810). After stirring for 5–6 hours, the mixture is discharged into 2% caustic soda solution (2300). More 1% caustic soda solution (1400) is added and after 4 hours' stirring, the formation of the dichloroindigo is complete. The dye is filter-pressed and excess acetone recovered from the filtrate. Dibromination is then effected by adding bromine (120 kg.) to the dichloroindigo (200) in methyl hydrogen sulfate (600) and, after stirring for a few hours, leading in chlorine (30) during 18–20 hours. The mixture is poured into water and the dyestuff collected, purified by boiling with dilute caustic soda solution, washed and standardized.



(I)



Brilliant Indigo 4G

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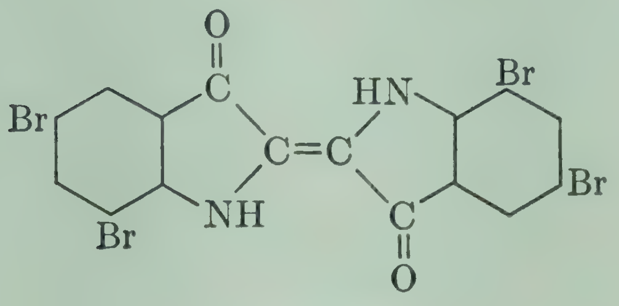
[35] *Ber.* **42,** 765 (1909); **55,** 1655 (1922).

[36] BASF, DRP 237,262.

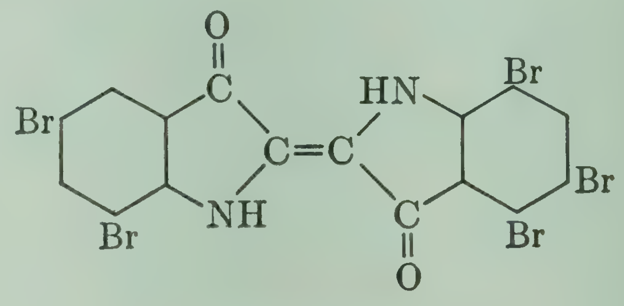
[37] *BIOS* **1482.**

[38] BASF, DRP 234,961.

5-Bromoindigo (Indigo RR, IG) (cf. CI 1182) and 5,5′-dibromoindigo (Indigo RB, IG) (cf. CI 1183) can be made by brominating indigo in nitrobenzene, sulfuric acid, or methyl hydrogen sulfate; IG use the last. Other brands, e.g., Indigo MLB/R and Indigo BASF/R, are mixtures of the mono- and dibromo compounds containing unbrominated indigo. Using the same solvents, raising the temperature and increasing the amount of bromine, three and four atoms may be introduced in the 5,7,5′- and 5,7,5′,7′-positions. The tri- and tetrabromo compounds, Ciba Blue B (CI 1183) and 2B (CI 1184), are important vat dyes, which are bright and level dyeing, and have good fastness properties. Brilliant Indigo 4B[37] (IG) is stated to be a mixture of tribromoindigo (1), tetrabromoindigo (1) and monochlorotribromoindigo (4). The pentabromo compound, Ciba Blue G (CI 1185), is prepared by bromination in concentrated or fuming sulfuric acid. On cotton, the brominated indigos are specially valuable in printing. The 6,6′-diamino derivative of Ciba Blue 2B, Ciba Brown R (CI 1187), prepared by the bromination of diaminoindigo, dyes cotton a chocolate brown fast to light, but not to chlorine; being dischargeable by chlorate, it is used in calico printing.



Ciba Blue 2B



Ciba Blue G

Miscellaneous derivatives. Nitro derivatives of indigo can be prepared by direct nitration.[39] The corresponding amines can be obtained by reduction, or synthetically from the appropriate aminated intermediates.

On heating indigo with benzoyl chloride in nitrobenzene solution in presence of copper powder, a remarkable transformation takes place and the product is a useful yellow vat dye, Indigo Yellow 3G (Ciba Yellow 3G) (Engi and Fröhlich, 1910; CI 1195).[40] Unlike the normal indigoid dyes, but like the anthraquinone vat dyes, it gives a reddish blue hydrosulfite vat, and Hope and Richter[41] have assigned the structure (II). Diesbach[42] prefers the constitution (III) for Indigo Yellow 3G. Three

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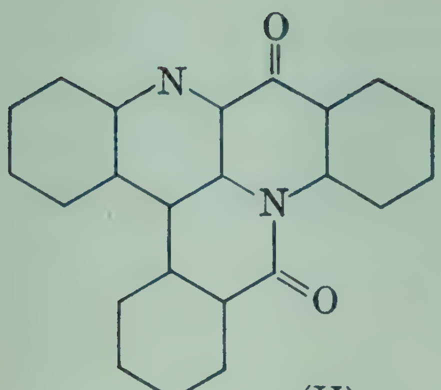
[39] van Alphen, *Rec. trav. chim.* **57,** 837 (1938).

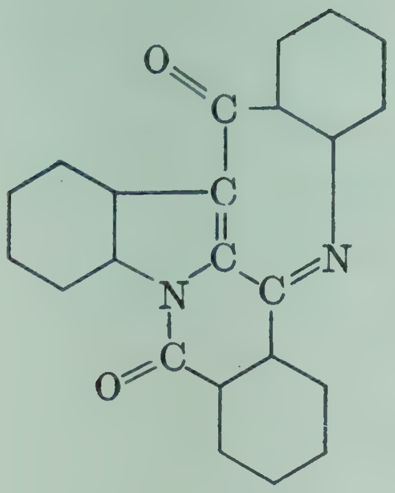
[40] Ciba, BP 29,368; MLB, 247,154–5; 248,250; 257,457; Engi, *Chem. Ztg.* **38,** 199 (1914).

[41] *JCS* 2783 (**1932**); 1000 (**1933**).

[42] Diesbach *et al.*, *Helv. Chim. Acta* **23,** 469 (1940); and earlier papers.



(II)



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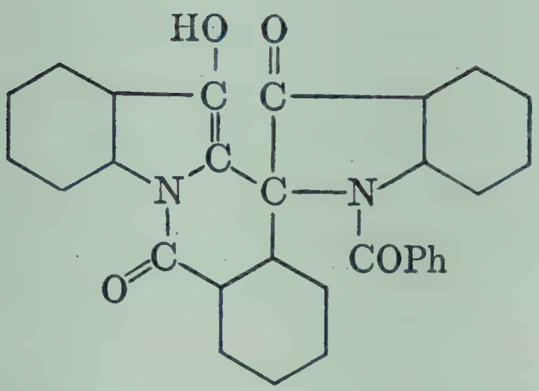
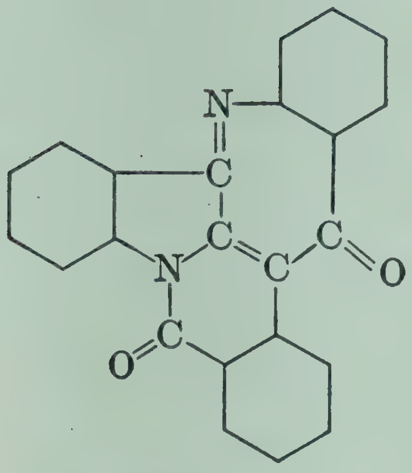


Hoechst Yellow R

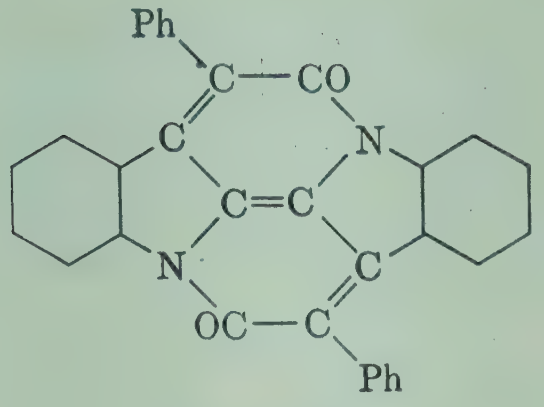


Hoechst Yellow U

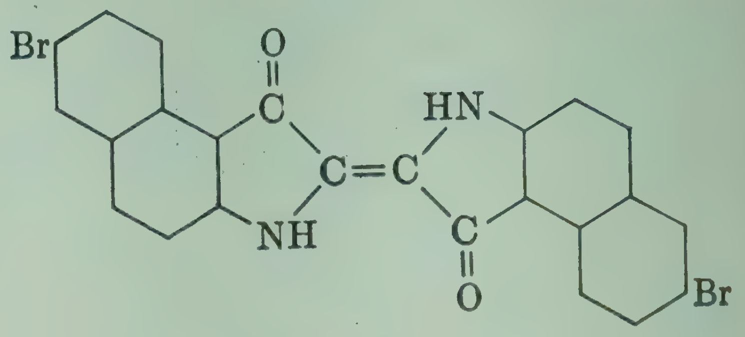
other compounds have been isolated from the products of the interaction of indigo and benzoyl chloride. One is colorless and is formed by treatment of indigo with boiling benzoyl chloride until the blue color disappears, or by treatment of *N*,*N*′-dibenzoylindigo with benzoyl chloride. It contains chlorine, which is replaced by hydroxyl on treatment with alkali, and this product is a new dye, Hoechst Yellow R, to which the indicated structure has been assigned by Diesbach.[43] The action of concentrated sulfuric acid converts Hoechst Yellow R into Hoechst Yellow U. The structures of these dyes must be regarded as provisional, and further proof is necessary. The action of phenylacetyl chloride on indigo in nitrobenzene does not give a vat dye, but a brilliant pigment, Ciba Lake Red B (CI 1194), which has excellent fastness to light. The action of benzoyl chloride on indirubin has also been studied.[44] Pure indirubin gives a monobenzoyl derivative, which has no active hydrogen; and technical indirubin, probably because of the catalytic action of impurities, gives tetrabenzoylleucoindirubin. Complex compounds are formed by further action.

[43] Diesbach *et al.*, *Helv. Chim. Acta* **24,** 158 (1941); **26,** 1869 (1943); **31,** 724 (1948); **32,** 1214 (1949).

[44] Diesbach *et al.*, *Helv. Chim. Acta* **28,** 690, 1387 (1945). For other interesting reactions of indigo and other indigoids, see Haller and Guyot, *Comp. rend.* **144,** 947 (1907); Diesbach and Heppner, *Helv. Chim. Acta* **32,** 687 (1949); Pummerer and Reuss, *Ber.* **80,** 242 (1947), and earlier papers.



Ciba Lake Red B



Ciba Green G

The four possible naphthalene analogs of indigo are all known, and they have no practical interest; but the dibromo derivative of bis-β-naphthindoleindigo, Ciba Green G (Engi, 1907; CI 1198), is a very bright green dye, used only in calico printing since it gives unlevel shades in dyeing. The method of preparation of Ciba Green G is interesting, being inapplicable to indigo itself; β-naphthylamine is condensed with oxalyl chloride to the oxamic acid which is cyclized to 2,1-naphthisatin by sulfuric acid, monobrominated, and converted into the dye by reduction of the α-chloride.

Indigoid coloring matters for cellulose acetate may be prepared on the same principles as in the azo and anthraquinone series by introduction of alkanolamine groups and their esters.[45]

Isatin and Thioisatin

Synthesis of isatin.[46] Isatin (yellowish red prisms, m.p. 203–205°) was first obtained (Erdmann, Laurent, 1841) by the oxidation of indigo with chromic or nitric acid. It can be prepared in 96% yield (calculated on the indigo consumed) by agitating a mixture of 20% indigo paste (100), sodium dichromate (13.5) and water (10) at 30°, and adding a solution of dichromate (13.5) and 91% nitric acid (37) in water (30) during 3–4 hours. The temperature must be maintained below 35°. After leaving overnight, the product is collected, washed, extracted with aqueous caustic soda, and filtered to recover unreacted indigo. Acidification of the alkaline solution gives isatin, which may be purified by crystallization from water or glacial acetic acid.[37, 47] Isatin and indoxyl react to form indirubin, and not indigo; but if isatin-α-anil is used instead of isatin, indigo is obtained. Sandmeyer developed a synthesis of isatin-2-anil (isatin-α-anilide; m.p. 126°) and he also showed that the anil could be converted directly into indigo by reduction with ammonium sulfide in alcoholic solution. Although the method was more expensive than the Heumann syntheses so far as indigo was concerned, it was useful for making isatin itself and isatin derivatives, which are important intermediates for the production of other indigoid and thioindigoid dyes. Sandmeyer's original synthesis (1899) of isatin from aniline (Chart 4) and indigo from isatin involved a long series of reactions,[48] and had the disadvantage of using hydrogen sulfide, an unpleasant and toxic gas, so that in spite of the good yields at every stage it was abandoned later (1919) in favor of a second and simpler synthesis of isatin, applicable to amines of the benzene series, also discovered by Sandmeyer (Chart 4).[49] When an aqueous solution of equimolecular amounts of aniline hydrochloride and chloral hydrate is boiled for a few minutes with hydroxylamine hydrochloride (about 3 moles), and cooled, isonitrosoacetanilide separates in 90% yield. When the dry product is dissolved in concentrated sulfuric acid, heated at 80° for a few minutes, cooled and poured into ice, isatin is obtained in about 80% yield.[50] Substituted isatins such as 6-chloro-7-methylisatin and 5-chloro-7-methoxy-4-methylisatin are conveniently prepared by the chloral-hydroxylamine method.[23] IG Hoechst employed a modification of the original Sandmeyer method; diphenyl cyanoformamidine was converted directly into isatin-2-anil, instead of proceeding through the thioamide stage.[23]

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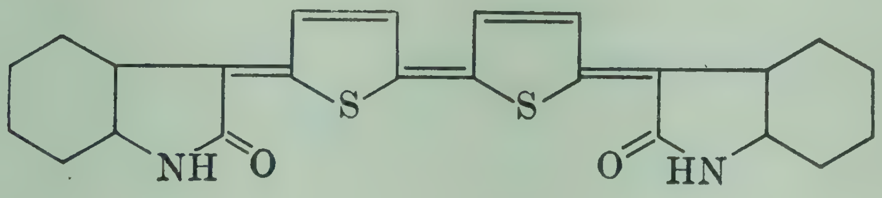
[45] Dickey, McNally, and Eastman-Kodak, USP 2,397,928.

[46] The chemistry of isatin has been reviewed by Sumpter, *Chem. Revs.* **34,** 393 (1944).

[47] Henesey, *J. Soc. Dyers Colourists* **53,** 347 (1937).

Isatin[51] dissolves readily in aqueous caustic soda solution on warming, and the lactam group opens with the formation of the sodium salt of isatinic acid. Isatin is also soluble in hot water, owing to the presence of a carbonyl in addition to the amide group. The β-carbonyl group exhibits the usual ketone reactions, and undergoes facile condensation with compounds containing reactive methylene groups. The blue indophenine, which provides a sensitive color test for thiophene in benzene, has the indicated structure.[52] 1,2-Diketone properties are modified by the implication of the α-carbonyl in an amide system. Treatment of isatin with phosphorus pentachloride results in enolization of the



Indophenine

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[48] For an account of this process, see Fierz-David and Blangey, Grundlegende Operationen der Farbenchemie, 5th ed., Springer, Wien, 1943, p. 307.

[49] Sandmeyer, *Helv. Chim. Acta* **2,** 237 (1919); Geigy, BP 128,122.

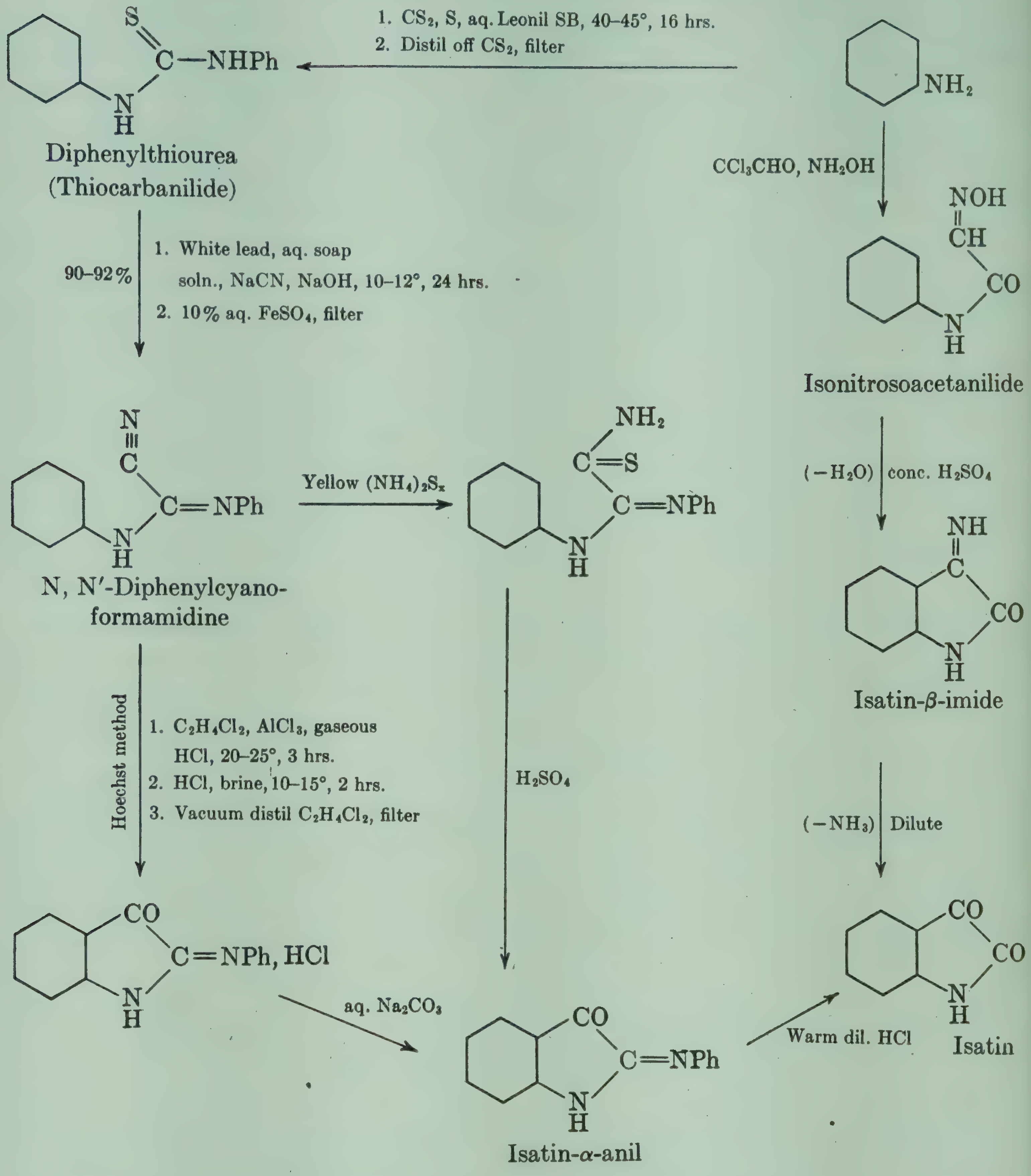
[50] Marvel and Hiers, *OSCV* I. For the preparation of hydroxylamine hydrochloride, see Semon, *OSCV* I.

[51] Heller, Über Isatin, Isatyd, Dioxindol, und Indophenin, Enke, Stuttgart, 1931.

[52] Steinkopf and Hanske, *Ann.* **541,** 238 (1939).

CHART 4

Sandmeyer Syntheses of Isatin


1. CS_2, S, aq. Leonil SB, 40–45°, 16 hrs.
2. Distil off CS_2, filter
NH_2
S
C—NHPh
N
H
Diphenylthiourea
(Thiocarbanilide)
CCl_3CHO, NH_2OH
NOH
CH
CO
N
H
Isonitrosoacetanilide
90–92%
1. White lead, aq. soap soln., NaCN, NaOH, 10–12°, 24 hrs.
2. 10% aq. $FeSO_4$, filter
N
C
C=NPh
N
H
N, N′-Diphenylcyanoformamidine
Yellow $(NH_4)_2S_x$
NH_2
C=S
C=NPh
N
H
(−H_2O) conc. H_2SO_4
NH
C
CO
N
H
Isatin-β-imide
Hoechst method
1. $C_2H_4Cl_2$, $AlCl_3$, gaseous HCl, 20–25°, 3 hrs.
2. HCl, brine, 10–15°, 2 hrs.
3. Vacuum distil $C_2H_4Cl_2$, filter
H_2SO_4
(−NH_3) Dilute
CO
C=NPh, HCl
N
H
aq. Na_2CO_3
CO
C=NPh
N
H
Isatin-α-anil
Warm dil. HCl
CO
CO
N
H
Isatin

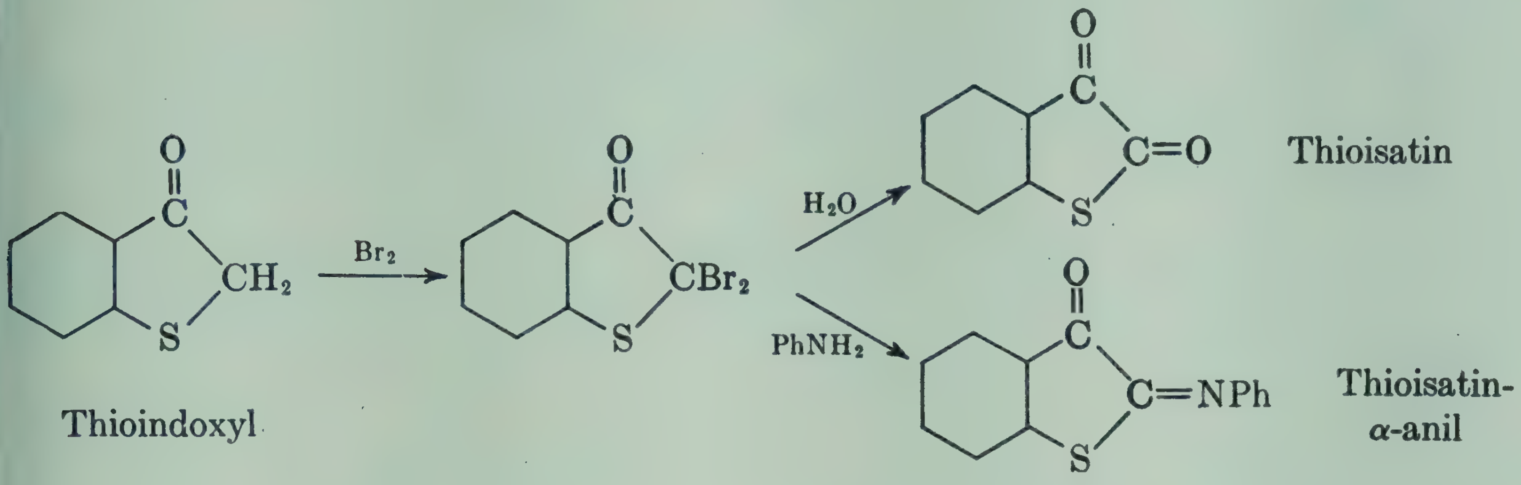
α-carbonyl and the formation of isatin chloride (see Chart 1), which condenses with indoxyl or thioindoxyl to 2,2′-indigos.

By adding bromine (153) and chlorine (42) successively to isatin (225) in dilute hydrochloric acid, maintaining the temperature below 17°, 5-bromoisatin is obtained in 95% yield.[23] Dibromination can be effected in concentrated sulfuric acid, raising the temperature gradually from −8 to 60°.[53] 5,7-Dibromoisatin crystallizes from alcohol in orange-red needles, m.p. 248–250°. 5,7-Dichloroisatin is produced in about 80% yield by chlorination in glacial acetic acid solution at 80°.

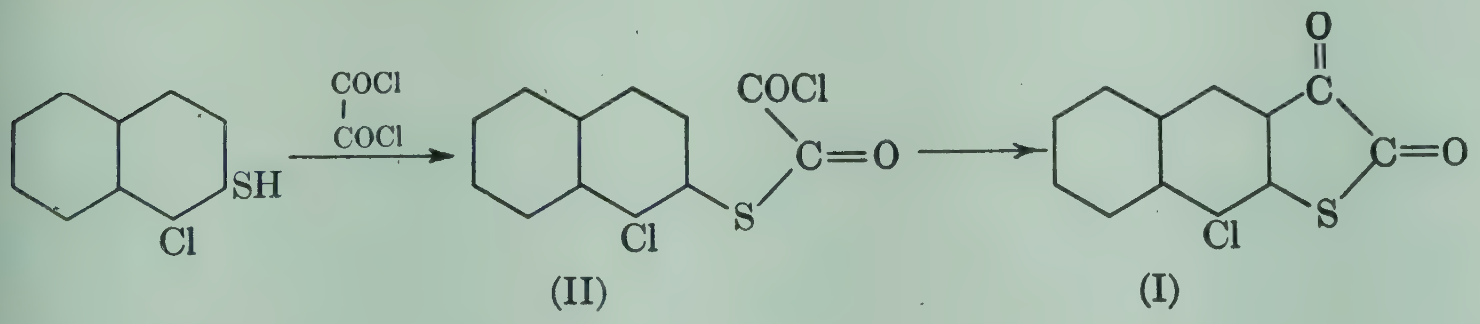
---

[53] *FIAT* **1313** II.

Thioisatin. The sulfur analog of isatin, thionaphthene-2,3-quinone (thioisatin), is prepared from thioindoxyl by bromination and hydrolysis. The dibromo compound can also be converted into the 2-anil by treatment with aniline. These sulfur compounds behave similarly to isatin and its 2-anil; thioisatin condenses with indoxyl or thioindoxyl to form the unsymmetrical or indirubin type of dye, while the 2-anil and the 2-chloride form the symmetrical or indigo type. It has been stated that with acenaphthenone and a few other compounds thioisatin itself condenses in the 2-position.[54] Mann *et al.* have shown that the condensation of thioindoxyls with the α- or the β-carbonyl group of thioisatin is mainly determined by the position of the substituents in the quinone molecule and is unaffected by substitution in the thioindoxyl component; indoxyl, on the other hand, always gives the β-condensation product.[55] Unsymmetrical or 2,3′-derivatives of thionaphthene, made by condensing thioisatin with suitable intermediates containing a reactive methylene group, have been mentioned in the patent literature, but apparently no dye of this type has been exploited commercially.



Naphththioisatins (e.g. I) can be prepared by condensing a thionaphthol with oxalyl chloride; the intermediate (II) cyclizes smoothly to the thiophene derivative.[56]

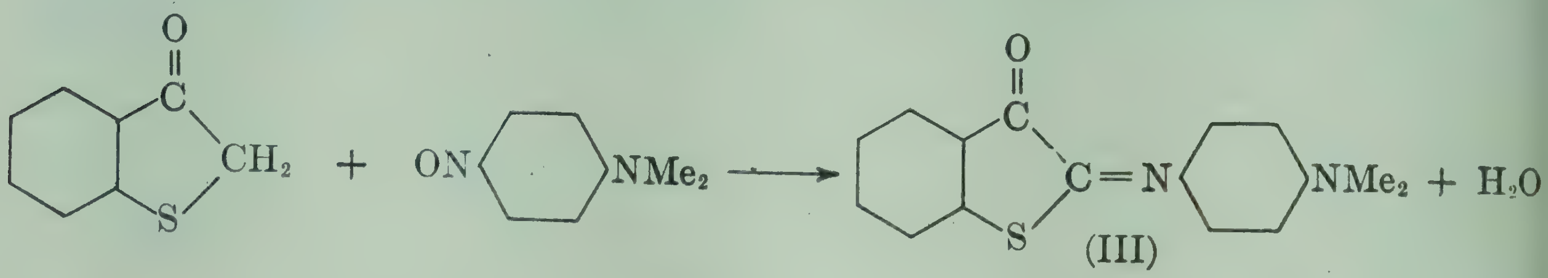


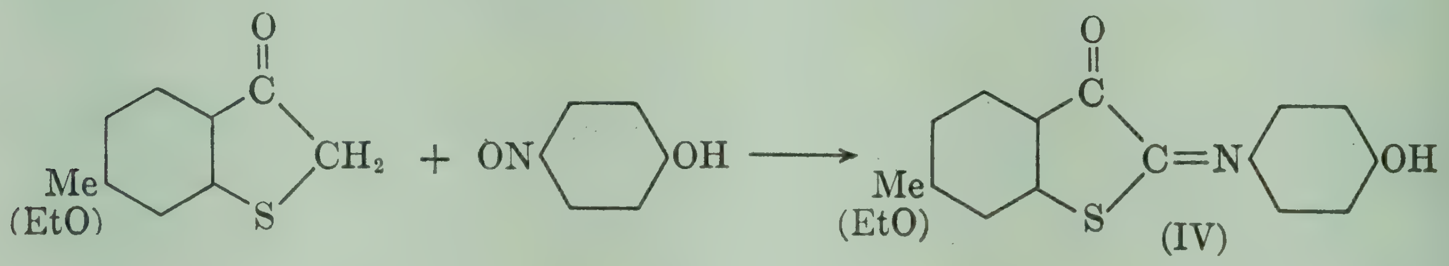
[54] Ciba, DRP 226,244.

[55] *JCS* 404 (**1942**); 893, 910 (**1945**).

[56] Ciba, BP 214,864.

A convenient route to thionaphthenequinone-anils is to condense thioindoxyl and its derivatives with aromatic nitroso-compounds, and the method has found practical application in the preparation of thioindigoid dyes from the thionaphthenequinone-anils as the intermediates. Thus thioindoxyl and *p*-nitrosodimethylaniline react readily to form (III).[57] Such anils themselves have been used as cellulose acetate dyes;[58] when 6-methyl- or 6-ethoxythioindoxyl is condensed with *p*-nitrosophenol, the anil (IV) and its *O*-methyl ether are both yellow dyes for cellulose acetate.





Selenium analogs of thioindoxyl and thioindigoid dyes have been described; selenoindoxyl is prepared by cyclizing phenylselenoglycollic acid o-carboxylic acid with acetic anhydride.

THIOINDOXYL AND ITS DERIVATIVES

The preparation of thioindoxyl is mentioned later as the intermediate for Thioindigo; but it is desirable at this stage to outline the methods of preparation of thioindoxyl derivatives, since these are important intermediates for the coloring matters to be described later. There are two main routes to thioindoxyls, as for indoxyls: cyclization of (1) arylthioglycollic acids; and (2) arylthioglycollic acid *o*-carboxylic acids. While phenylthioglycollic acid does not give a good yield of thioindoxyl, substituted thioindoxyls can be conveniently prepared by this method. Thus, 5,6,7-trichlorothioindoxyl is prepared from 1,2,3-trichlorobenzene as shown in Chart 5. The thiophenols, required for conversion into arylthioglycollic acids, can also be prepared by diazotizing the appropriate amine, heating with sodium disulfide, and reducing the diaryldisulfide with iron and acid. The second route to thioindoxyls, illus-

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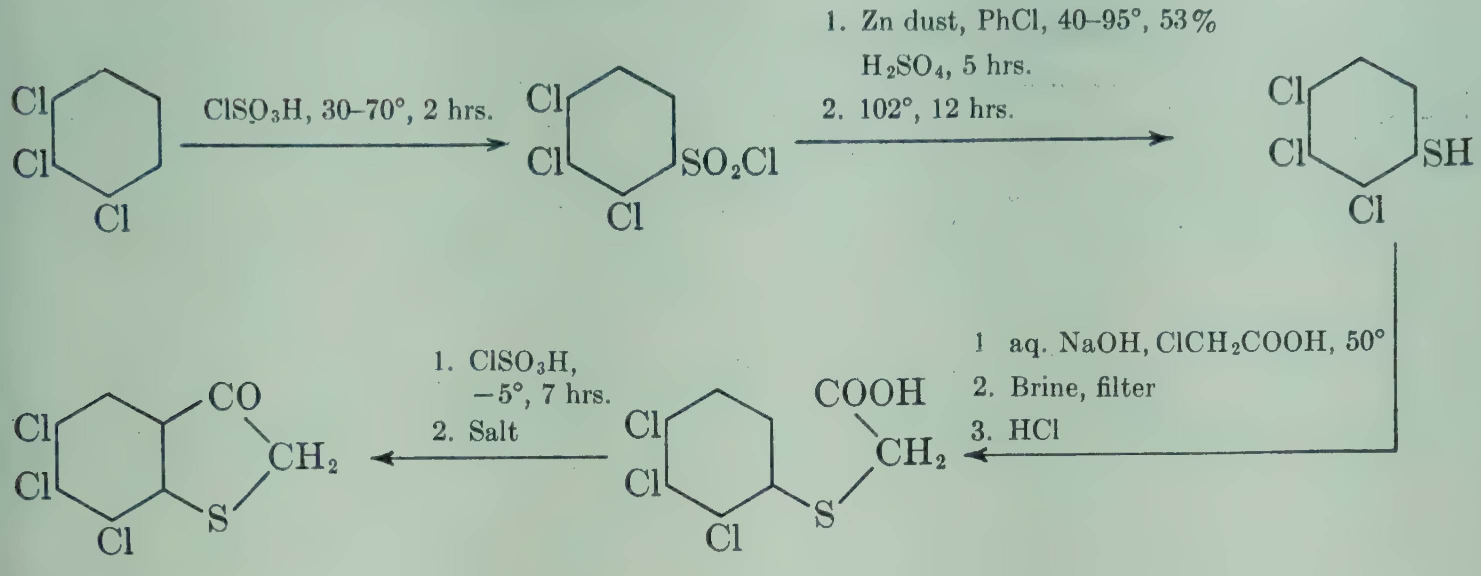
[57] BASF, BP 17,498/1908; Pummerer, *Ber.* **43**, 1370 (1910).

[58] Havas and du Pont, USP 2,127,483–4.

CHART 5

PREPARATION OF 5,6,7-TRICHLOROTHIOINDOXYL



5, 6,7-Trichloro-
thioindoxyl

trated in Chart 6 by the preparation of 6-methoxythioindoxyl from *p*-anisidine,[59] involves the Herz reaction for making the *o*-aminothiophenol derivative (I), and its conversion into the thioindoxyl via the nitrile (II). The Herz reaction (Cassella, 1914)[60] is very important as a method for preparing *o*-aminothiophenols, which are useful not only as intermediates for thioindigoid dyes, but also for the synthesis of sulfur dyes of authentic constitution.[61] For the preparation of 6-methoxythioindoxyl, a mixture of *p*-anisidine hydrochloride (224), sulfur chloride (400) and chlorobenzene (1120) is heated at 93° for 2 hours, cooled and filtered. The product (6-methoxybenzo-1,3-thiaza-2-thionium chloride; III) is freed from chlorobenzene by heating at 70° under vacuum, and hydrolyzed to the thiol (I) by agitation with water (1000), ice (5000) and chalk (205) for 10 hours at 5°. Chloroacetic acid (160), 26.8% caustic soda solution (680) and zinc dust (56) are added, together with ice and water to make up the volume to 5000 l; the temperature is maintained at 10°, and then gradually raised to 25°. After agitation until the condensation is complete, the alkaline solution of the thioglycollic acid (IV) is screened, and the filtrate is diazotized in the usual manner with sodium nitrite and hydrochloric acid. The diazonium solution is run into a solution of sodium cuprochloride (copper dissolved in hydrochloric acid, sodium chloride and a little chlorate), cyanide and bicarbonate at 11°. The nitrile (II) is converted into the ketimine (V) by adding sodium tetrasulfide solution to precipitate copper, then enough strong caustic

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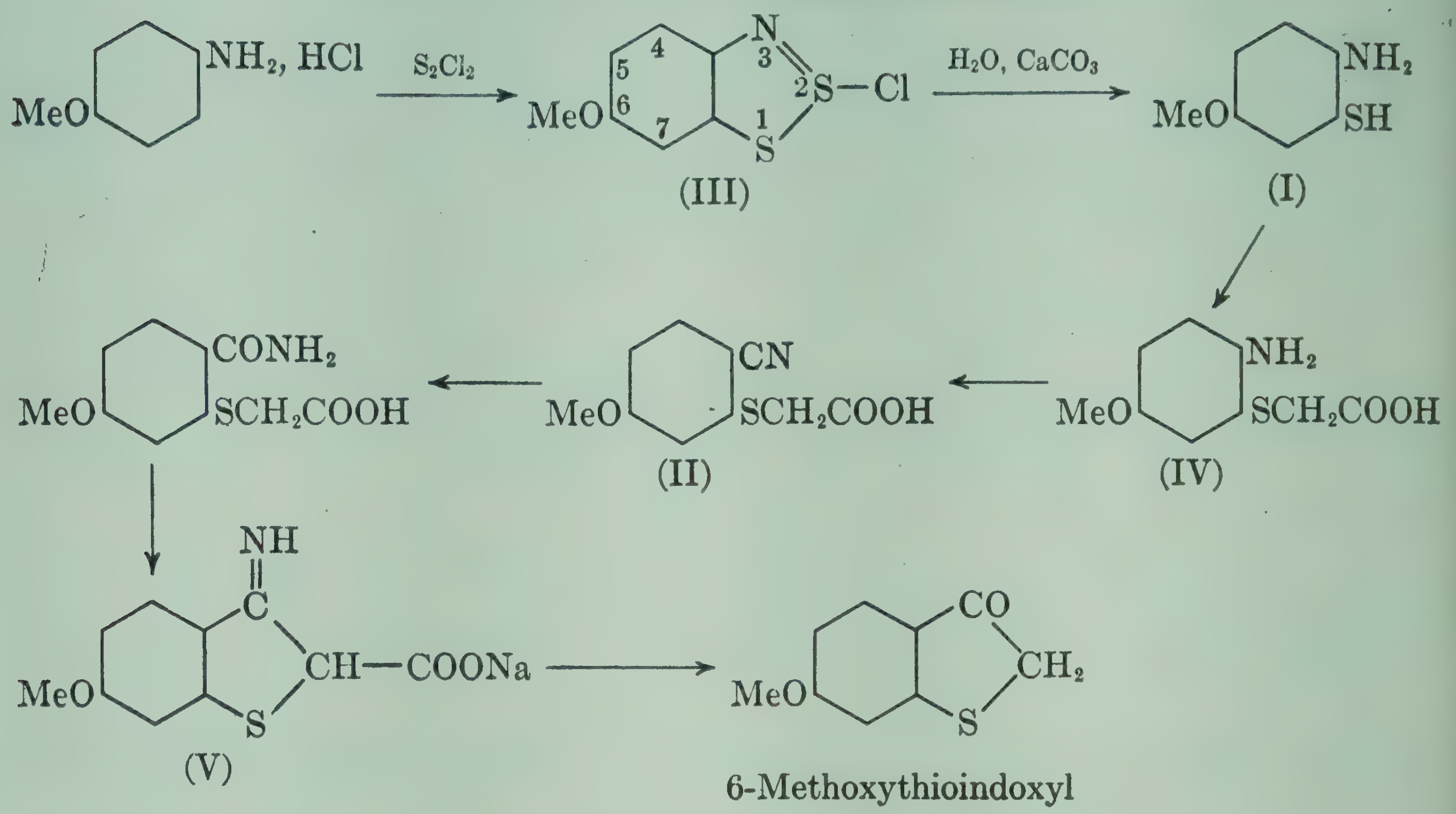
[59] *BIOS* **1156**.

[60] DRP 360,690; USP 1,243,170; See also Hixon and Cauwenberg, *JACS* **52**, 2118, 2125 (1930).

[61] See Chapters XXXV and XXXVI.

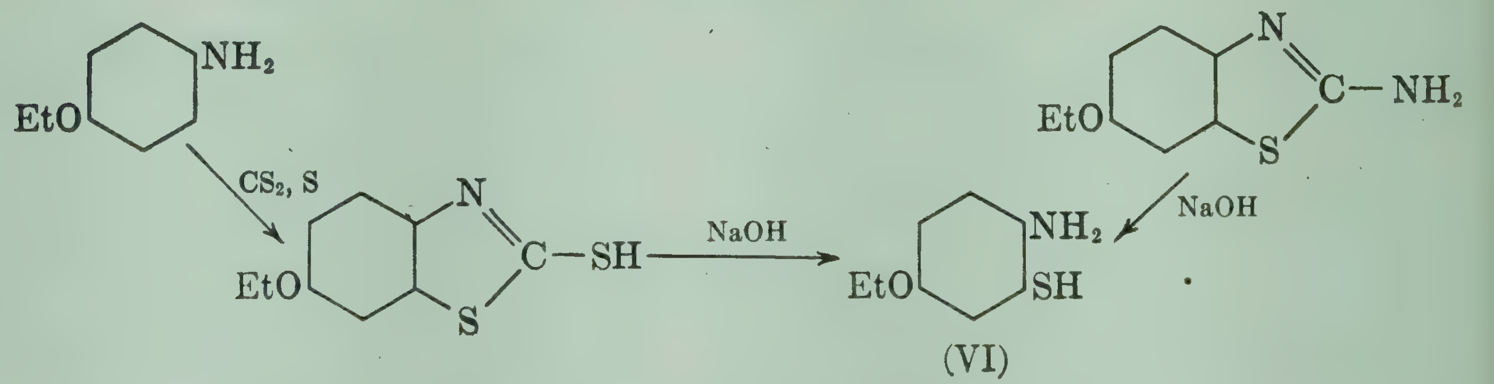
CHART 6

Preparation of 6-Methoxythioindoxyl


MeO
NH₂, HCl
S₂Cl₂
N
S—Cl
1 2 3 4 5 6 7
(III)
H₂O, CaCO₃
NH₂
SH
(I)
CONH₂
SCH₂COOH
CN
SCH₂COOH
(II)
NH₂
SCH₂COOH
(IV)
NH
C
CH—COONa
S
(V)
CO
CH₂
S
6-Methoxythioindoxyl

soda solution to make a 3% solution and sodium chloride to make a 15% solution, and heating at 60° for 4 hours. The product (V) is salted out, filtered, dissolved in sodium carbonate solution and filtered to remove copper sulfide. The filtrate is acidified with sulfuric acid and heated at 70°. On cooling to 20°, the thioindoxyl separates in a yield of about 55% calculated on *p*-anisidine.

o-Aminothiophenols can be prepared by treating an arylthiourea with halogen to form a 2-aminobenzothiazole, and breaking up the thiazole ring with alkali.[62] 2-Amino-5-ethoxythiophenol (VI) has also been prepared[63] by a method devised by Hofmann[64] in 1887, consisting in the alkali fusion of 2-mercaptobenzothiazoles at 180–185°. 2-Mercaptobenzothiazole itself is an extensively used rubber accelerator, and this compound and its nuclear substituted derivatives are prepared by heating arylamines with carbon disulfide and sulfur in an autoclave at 200°.


EtO
NH₂
CS₂, S
N
C—SH
S
NaOH
NH₂
SH
(VI)
N
C—NH₂
S
NaOH

---

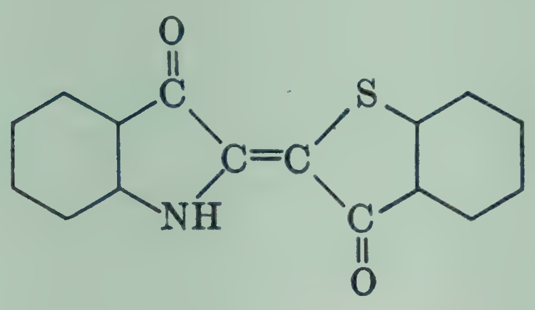
[62] ICI, BP 361,306.

[63] du Pont, BP 423,869.

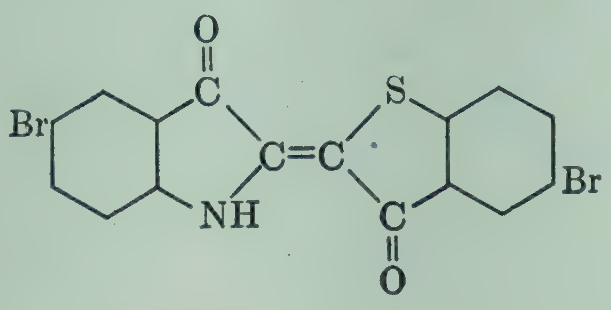
[64] Hofmann, *Ber.* **20,** 1788 (1887).

2-INDOLE-2′-THIONAPHTHENE-INDIGOS

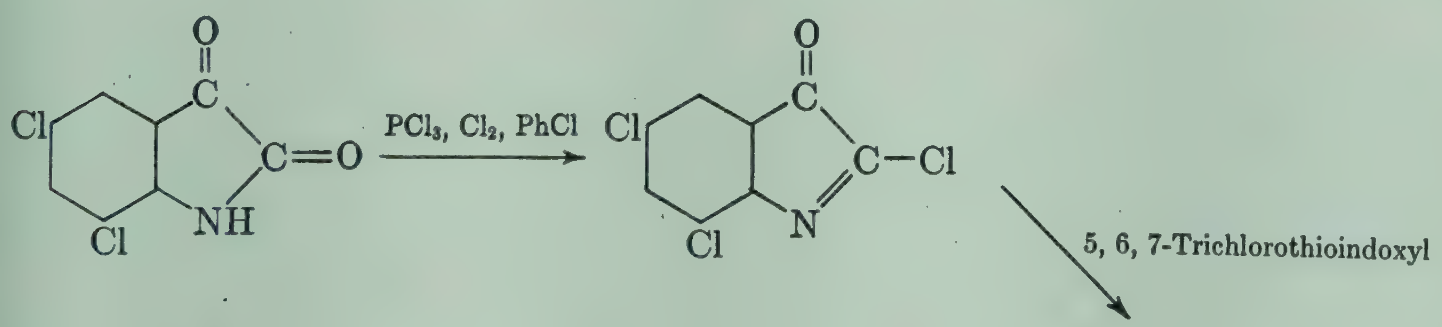
Dyes of this class are also called hemithioindigos. Ciba Violet A (Engi, 1906), prepared by condensing isatin-α-anilide with thioindoxyl, is no longer used, but the 5,5′-dibromo compound, Ciba Violet 3B (Cb; CI 1221), and the 5,7,5′-tribromo compound, Ciba Violet B (Cb; CI 1222), are more useful. The monobromo compound, Ciba Gray G (CI 1220), dyes cotton blue, converted into a fast gray by aftertreatment with soap and soda ash. The pentachloro derivative, Indanthrene Printing Violet BBF (IG), has good light fastness and is a useful printing color; it is made by condensing 5,7-dichloroisatin chloride with 5,6,7-trichlorothioindoxyl by a general procedure applicable to dyes of this type (2,2′-indigos). The isatin chloride is prepared by adding the isatin (1 mole) to phosphorus trichloride (1.3) and chlorine (1.34) in chlorobenzene, and heating to 125° in one hour. This solution is cooled to 100° and added to a solution of the thioindoxyl (1 mole) in chlorobenzene at 65°. The mixture is cooled to 45° (one hour); the precipitated dye is filtered and washed with chlorobenzene; and the solvent is removed by steam distillation. The dye is filtered from the aqueous suspension, dried, dissolved in 95% sulfuric acid, and reprecipitated by blowing into

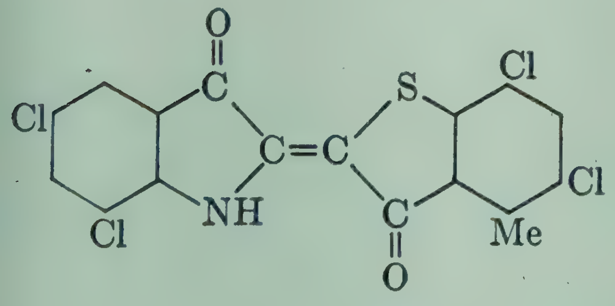


Ciba Violet A

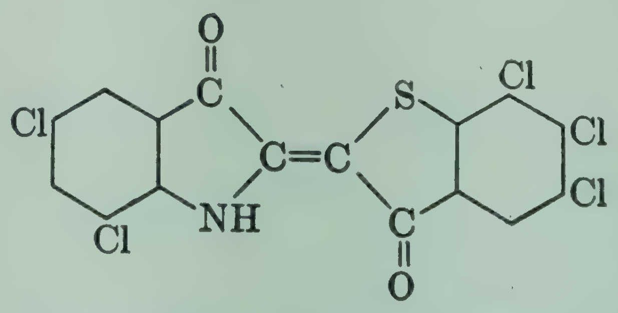


Ciba Violet 3B



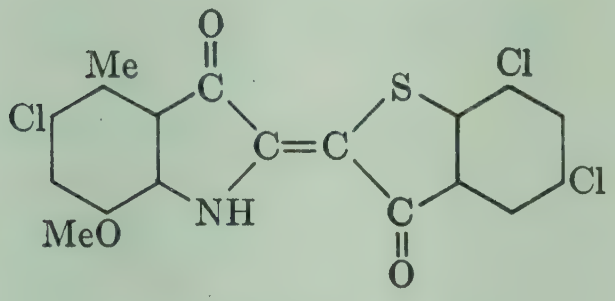


Algol Violet BBN

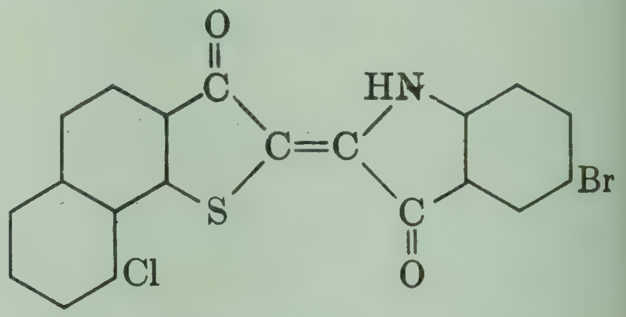


Indanthrene Printing Violet BBF

water. The dye is again filtered off, washed acid-free, and standardized.[59, 65] Algol Violet BBN, which has good all-round fastness, is made similarly. The 6-chloro-4-methylthioindoxyl analog of Algol Violet BBN is Vat Violet RR, not used as such, but for conversion into Indigosol Violet IRR.[33] Indanthrene Printing Blue B (IG, 1930) is the product of the condensation of 5-chloro-7-methoxy-4-methylisatin chloride with 5,7-dichlorothioindoxyl.[59] Algol Brown 3R (ST 1338) (light fastness 4; soda boil 2–3) is a bromination product of 2-indole-2′-(6′-amino)thionaphthene-indigo. Indanthrene Printing Black BL (IG, 1931) is made by condensation of 9-chloro-(6′,7′-)benzothioindoxyl with 5-bromoisatin chloride; cyclization of 8-chloro-1-naphthylthioglycollic acid by phosphorus trichloride and aluminum chloride in chlorobenzene solution gives the former intermediate. Using isatin chloride instead of 5-bromoisatin chloride in this condensation, the product is Indanthrene Printing Black BGL; using 5,7-dibromoisatin chloride, the product is Indanthrene Printing Black F. Indanthrene Printing Black BL, shaded with small amounts of Indanthrene Golden Yellow RK and Indanthrene Dark Brown 5R, is marketed as Indanthrene Printing Black TL.[59]

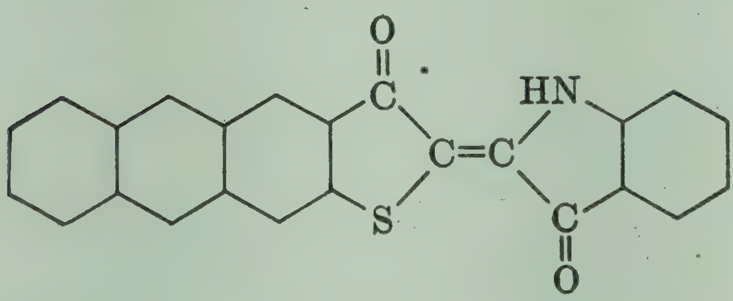


Indanthrene Printing Blue B

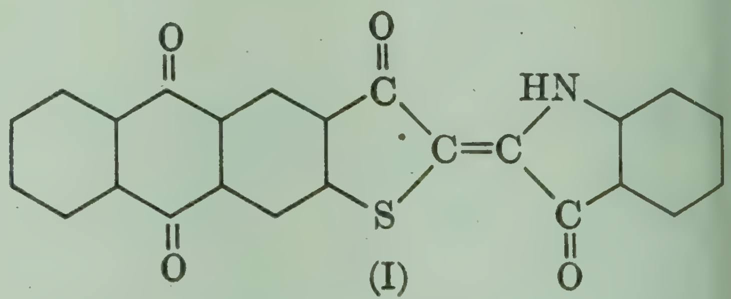


Indanthrene Printing Black BL

Mayer (Cb) has described a series of hemithioindigoid dyes prepared by condensing isatin-α-anilide with the anthracene and anthraquinone analogs of thioindoxyl. Cibanone Green GC (Mayer and Würzler, 1923) is an example. The anthraquinone analog (I) is a blue dye. While these are 2,3-substituted anthracene derivatives, red-brown, violet and black dyes prepared from the 1,2- and 2,1-compounds have also been described.



Cibanone Green GC



(I)

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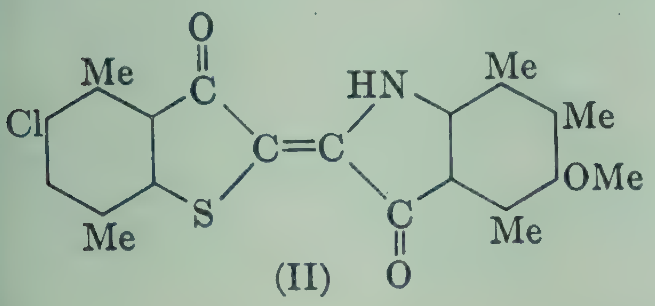
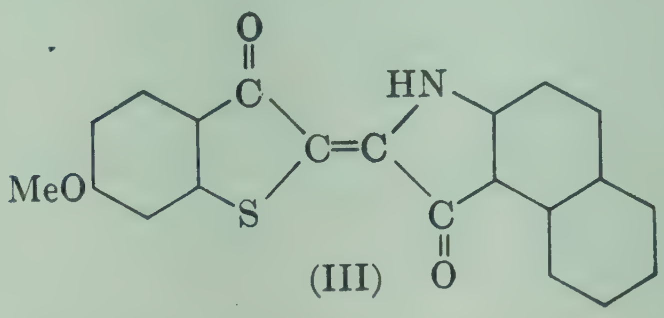
[65] *BIOS* **983**.

Substitution of both 5 and 6 positions in thioindoxyl is described by Ciba, who condense 5-chloro-6-methyl-, 6-chloro-5-methyl-, and 5,6-dihalogeno-thioindoxyl with appropriate intermediates to give unsymmetrical dyes covering a wide range of shades.[66] IG also prepare heavily substituted unsymmetrical dyes starting with, for instance, 7-bromo-5-methoxy-4,6-dimethylisatin. The violet dye (II) is claimed to be free from the defect of changing color on wool when spotted with water.[67] The introduction of naphthalene nuclei in these dyes often leads to olive, brown, and green shades. The compound (III) dyes cotton olive green of light fastness 7, and such dyes are useful in printing.[68] The methoxyl group may be in the naphthalene nucleus; for instance 6-methoxy-2,1-naphthisatin condensed with 6,7-benzothioindoxyl gives a greenish-olive;[69] or it may be in the naphthalene nucleus on the naphththiophene side.[70]


(II)


(III)

2,2′-*bis*THIONAPHTHENE-INDIGOS

Friedländer's discovery (1905)[71] of Thioindigo Red B (CI 1207), the sulfur analog of indigo, was a very important stage in the history of the indigoid dyes, since it led to the synthesis of a large number of derivatives and of similar dyes[59, 65] which are largely employed in dyeing and printing. Several are useful as solubilized vat colors (Indigosols), because they yield bright attractive shades in printing and they lend themselves better than the anthraquinone vat dyes to the older method of preparing Indigosols.[33]

While Indigo may be manufactured alternatively from phenylglycine or its *o*-carboxylic acid, Thioindigo is made only from phenylthioglycollic acid *o*-carboxylic acid (I). Starting from anthranilic acid, the route to (I) is shown in Chart 7.[72] The cyclization of (I) to thioindoxylic acid

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[66] Ciba, BP 372,640; 380,020; 389,350.

[67] IG, BP 396,636.

[68] IG, BP 383,543.

[69] IG, BP 380,902.

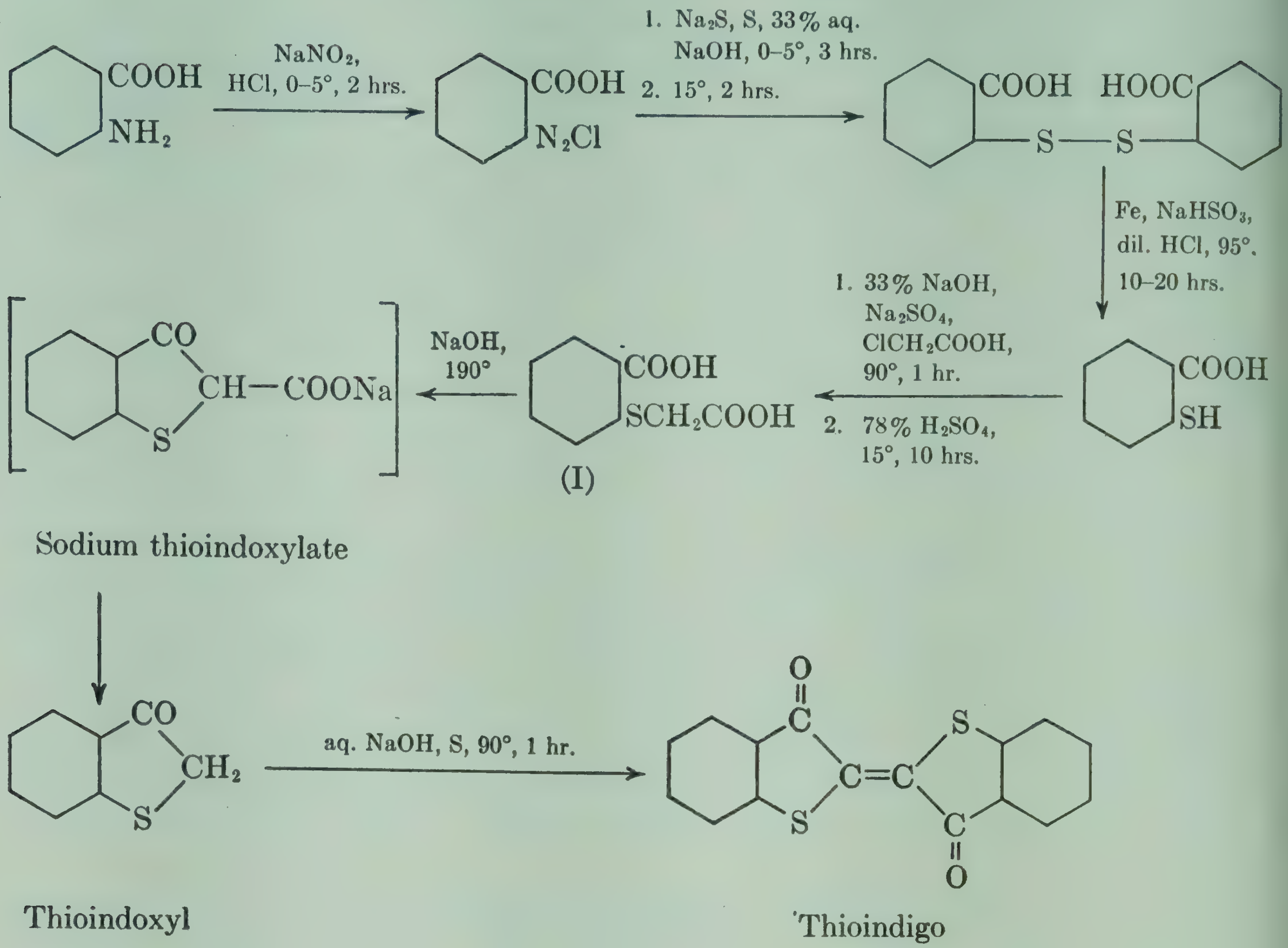
[70] IG, BP 383,662.

[71] *Ber.* **39,** 1060 (1906).

[72] For details of the route through thiosalicylic acid, see Allen and Mackay, *OSCV* II; see also Ref. 23.

CHART 7

PREPARATION OF THIOINDIGO

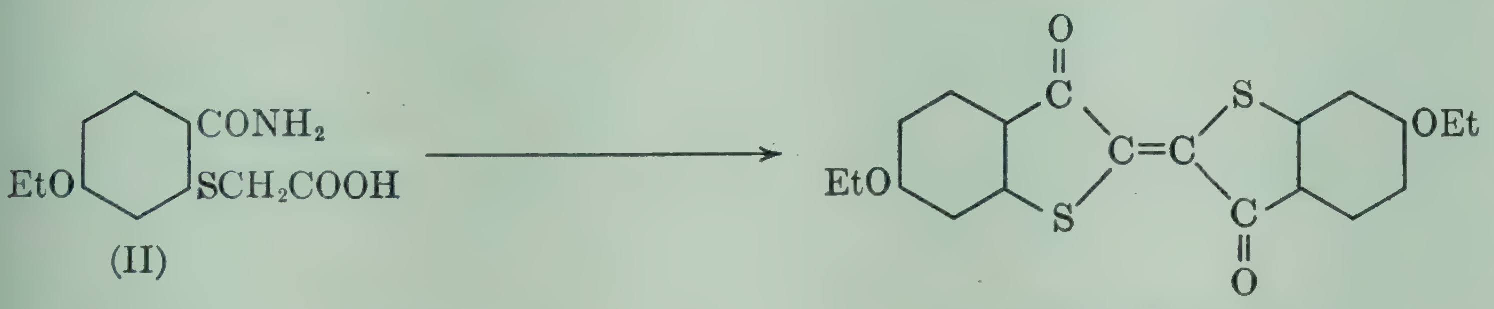

COOH
NH₂
NaNO₂,
HCl, 0–5°, 2 hrs.
COOH
N₂Cl
1. Na₂S, S, 33% aq.
NaOH, 0–5°, 3 hrs.
2. 15°, 2 hrs.
COOH
HOOC
S
S
Fe, NaHSO₃,
dil. HCl, 95°,
10–20 hrs.
COOH
SH
1. 33% NaOH,
Na₂SO₄,
ClCH₂COOH,
90°, 1 hr.
2. 78% H₂SO₄,
15°, 10 hrs.
COOH
SCH₂COOH
(I)
NaOH,
190°
CO
CH—COONa
S
Sodium thioindoxylate
CO
CH₂
S
Thioindoxyl
aq. NaOH, S, 90°, 1 hr.
O
C
S
C=C
S
C
O
Thioindigo

proceeds much more readily than the corresponding reaction for indoxylic acid; the decarboxylation is facile in both cases. Thioindoxyl crystallizes from water in needles, m.p. 71°, and closely resembles α-naphthol in odor and general properties. In the IG process for Thioindigo, (I) (106 parts as 50% paste) is added to caustic soda (225) and water (50) at 80°, the temperature raised slowly to 190°, and the fusion carried out at this temperature for 4 hours. The cooled melt is taken up in water, the alkalinity reduced to 4% by the addition of sulfuric acid, and oxidation of thioindoxyl to thioindigo effected by heating the solution with flowers of sulfur (98; made into a paste with Monopole Brilliant oil) at 90° during one hour. Using a good quality of (I), which is a critical factor, the yield is 78%.[65] An interesting feature in the synthesis of thioindigoids is the use of sulfur or sodium tetrasulfide for the oxidation of thioindoxyl and its derivatives.

Thioindigo (Ciba Pink B; Helindone Red BB; Algol Red 5B) can be vatted both by means of sodium sulfide and hydrosulfite-alkali; it is level dyeing, and yields a range of pale pink to bluish red shades which are equally fast, but the stronger shades are not very attractive. Thioindigo was formerly used for the production of pinks and reds in sunshade coverings and other fabrics requiring high fastness to light and weathering, but the dye is now obsolete. The thioindigo molecule is characterized by great stability, for instance to strong oxidizing agents; but Thioindigo is more readily reduced to the leuco derivative than indigo. The leuco compound is more stable than Indigo White, is less easily oxidized to the parent dye, and can be isolated as pale yellow crystals, sparingly soluble in water. The fastness figures for Thioindigo Red are light 5–6 and chlorine 4–5; the fastness to alkali boil is poor (2).

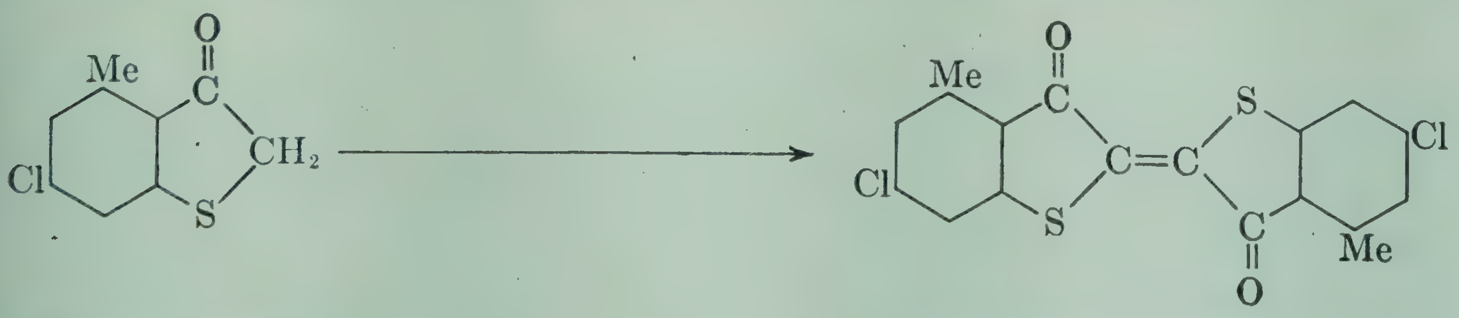
Derivatives of Thioindigo. The color is changed by substituents even more than with indigo. Thus the 5,5′-dibromo derivative is bordeaux (Ciba Bordeaux B; CI 1208). Derivatives containing alkyl, amino, hydroxyl, methoxyl and thioether groups have widely different shades. When the substituents are *para* to the sulfur atoms, the shade is changed to red, violet and deeper shades; when they are *para* to the carbonyl groups, the color is orange, orange-brown or pink.

Algol Orange RF is the 6,6′-diethoxy derivative of Thioindigo, prepared from (II) by treatment first with aqueous caustic soda and caustic potash at 110–145°, and then with flowers of sulfur at 95–100°. The amide (II) is prepared from *p*-phenetidine-3-sulfonic acid via the nitrile and the sulfonyl chloride.[23] Dibromination of Algol Orange RF gives Algol Scarlet GGR (ST 1352). An important member of this group is Indanthrene Brilliant Pink R, a bright, attractive dye with good fastness properties on cotton (light 5 and 4–5 for other agencies). 6-Chloro-4-methylthioindoxyl is oxidized to the dye by heating with aqueous caustic soda and sodium tetrasulfide at 85°.[65] The intermediate is prepared from *o*-toluidine by using the Herz reaction as described for 6-methoxy-



(II)

Algol Orange RF

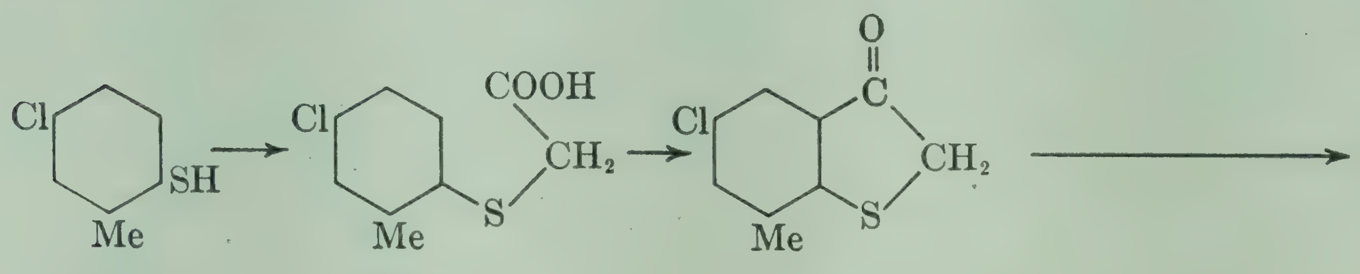


6-Chloro-4-methylthioindoxyl

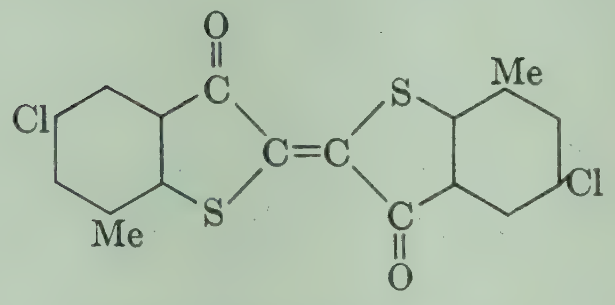
Indanthrene Brilliant Pink R

thioindoxyl; the action of sulfur chloride on *o*-toluidine effects nuclear chlorination (*para* to nitrogen) simultaneously with cyclization to the benzothiazathionium chloride. The bromine analog of Indanthrene Brilliant Pink R is Algol Pink B (ST 1353).

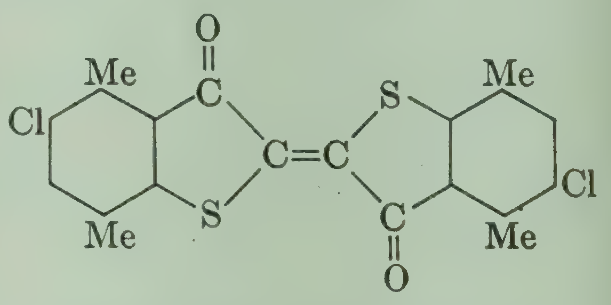
Indanthrene Red Violet RH is a dye which finds considerable use in spite of its being inferior to the anthraquinone vat dyes in its fastness to light (5) and to alkali boil. It is prepared by cyclizing the thioglycollic acid (IV) to the thioindoxyl (V) with chlorosulfonic acid at −5° and oxidizing (V) with bromine in chlorosulfonic acid at the same temperature, maintained by the use of solid carbon dioxide. The thiophenol (III), required for conversion into (IV), may be prepared from *m*-chlorotoluene via the sulfonyl chloride, or from 5-chloro-*o*-toluidine (Fast Red TR Base) via the diazonium salt and the disulfide. The latter route was used by IG after 1940.[53] According to CI 1212, Durindone Red 3B (BDC) and Thioindigo Red 3B (K) are constituted as 5,5′-dichloro-6,6′-dimethylthioindigo, and the same structure is assigned to Indanthrene Red Violet RH. Indanthrene Red Violet RRN (fastness: light 5, chlorine 5, other agencies 4) is made from monochloro-*p*-xylene via the sulfonyl chloride and the thiophenol.



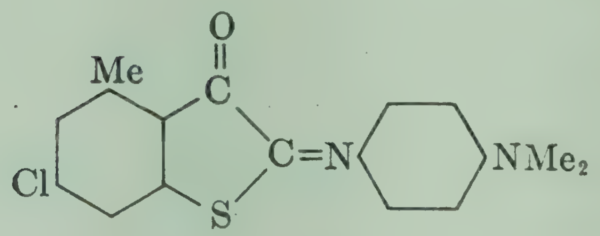
(III) (IV) (V)



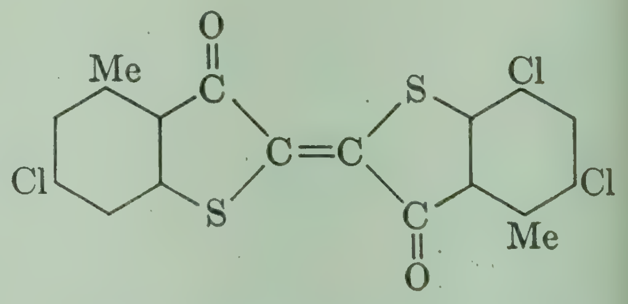
Indanthrene Red Violet RH



Indanthrene Red Violet RRN

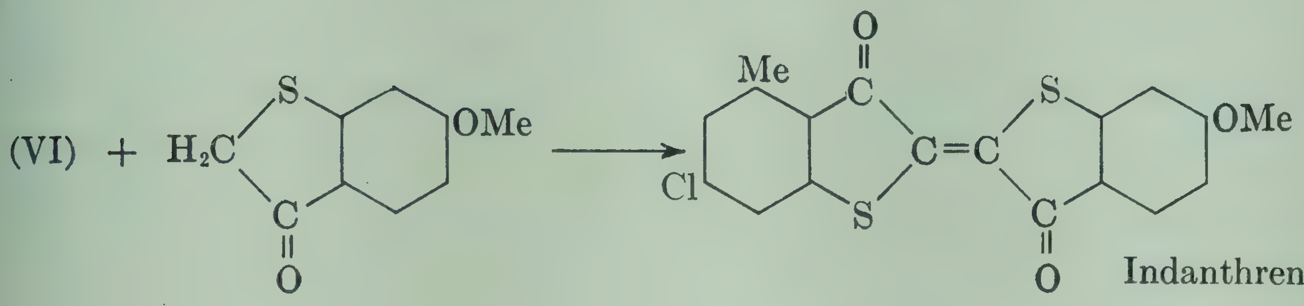


(VI)

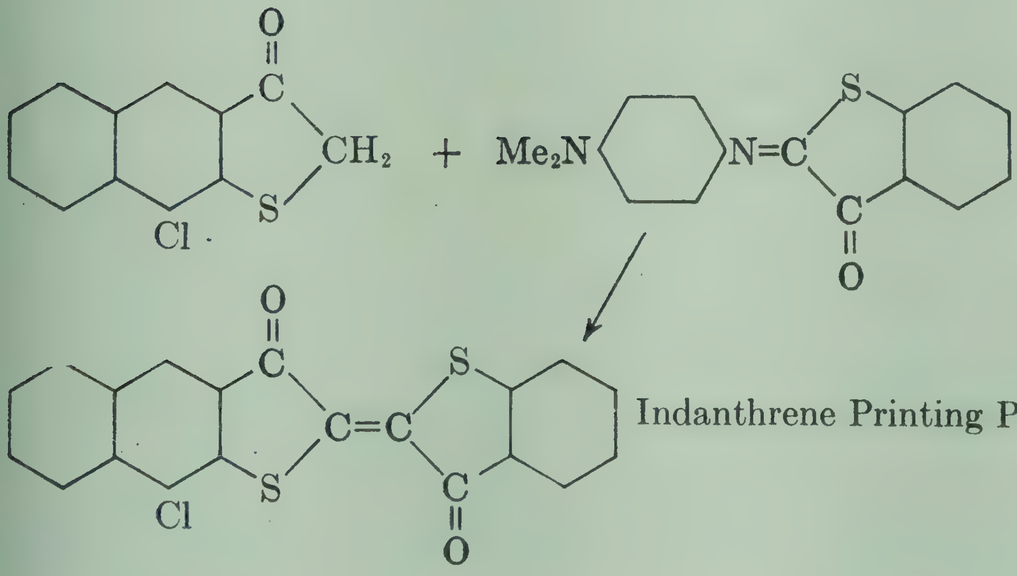


Indanthrene Brilliant Pink 3B

Algol Violet RR (ST 1351), 5,5'-dichloro-7,7'-dimethoxy-4,4'-dimethylthioindigo, is fast to chlorine (4–5), but has only moderate light fastness (4). Indanthrene Printing Pink FFB (6,6'-dichloro-4-methylthioindigo) and Indanthrene Brilliant Pink 3B are unsymmetrical derivatives of Thioindigo, which are made by the interaction of the appropriate pair of thioindoxyl derivatives.[59] Thus 6-chloro-4-methylthioindoxyl is converted into the anil (VI) by treatment with *p*-nitrosodimethylaniline in aqueous solution under faintly alkaline conditions at 25° for 24 hours. The anil (VI) and 5,7-dichloro-4-methylthioindoxyl are heated in chlorobenzene solution at 150° for 2 hours; Indanthrene Brilliant Pink 3B separates on cooling.[59, 73] An unsymmetrical thioindigoid dye containing an alkoxy group is the largely used Indanthrene Scarlet B, which has very good all-round fastness (light 6, chlorine 5, alkali boil 3–4). Indanthrene Printing Purple R is prepared by condensing 5,6-benzo-7-chlorothioindoxyl (prepared by aluminum chloride cyclization of 1-chloro-2-naphthylthioglycollic acid chloride) with the *p*-dimethylaminoanil of thioindoxyl in boiling chlorobenzene. Vat Brown IVD, another dye of this type, is not used as a vat dye, but converted into the solubilized derivative, Indigosol or Anthrasol Brown IVD.[33] These unsymmetrical dyes are stated to give more valuable shades with better light fastness than the analogous symmetrically constituted dyes.[74]



Indanthrene Scarlet B



Indanthrene Printing Purple R

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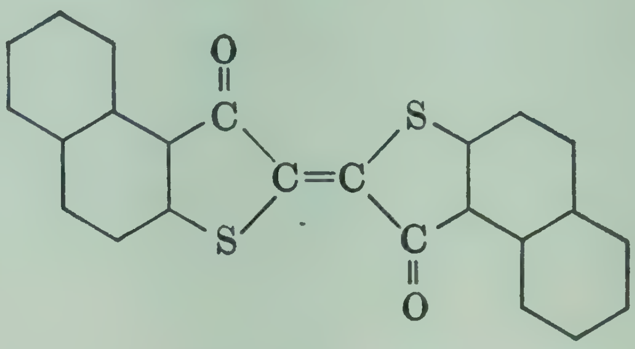
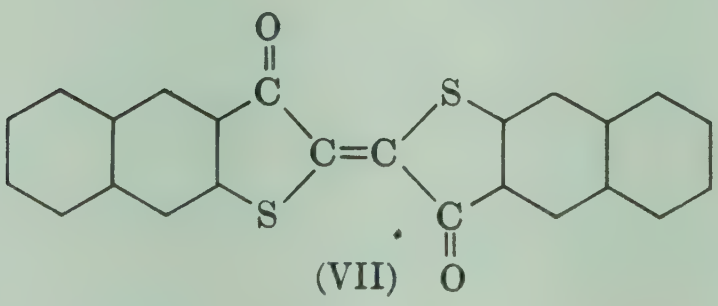
[73] See also IG, BP 355,661–2; 357,593; 359, 426.

[74] IG, BP 441,548.

7,7′-Diaminothioindigo, marketed at one time as Indanthrene Gray 6B (CI 1213), has excellent light fastness (7), but poor chlorine fastness (1–2). A dye of high all-round fastness among the thioindigoids used as cotton dyes is Indanthrene Brown RRD, which is valuable as a printing color and for conversion into the corresponding Indigosol. This naphthalene analog of Thioindigo Red is made by cyclization of β-naphthylthioglycolic acid to the benzothioindoxyl (2,1-naphththioindoxyl) by means of phosphorus trichloride and aluminum chloride in chlorobenzene solution, and oxidation of the thioindoxyl in alkaline solution by means of copper sulfate and atmospheric oxygen at 80°. Shades of improved clarity have been claimed by the cyclization of β-naphthylthioglycolic acid chloride with aluminum chloride, and subsequent vatting and reoxidation of the product.[75] Other thioindigos derived from naphthalene have also been described. The linear analog (VII) of Indanthrene Brown RRD is bluish green in color; the mixed type (VIII) is dark blue. The linear dye from anthracene is green, and the angular dyes are brown. The linear dye from anthraquinone is gray-blue, and the angular brownish-gray.



Indanthrene Brown RRD



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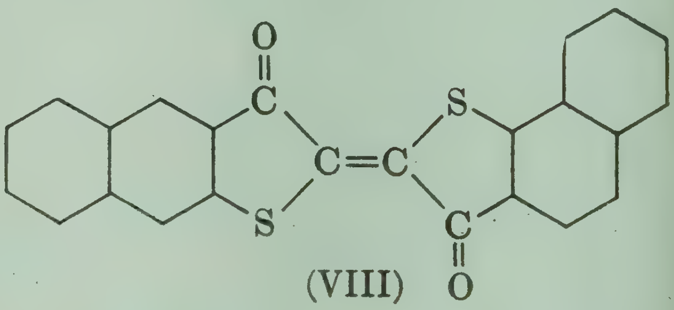

(VIII)

There is an extensive patent literature on thioindigo derivatives. Dyestuffs of the 2,2′-thioindigo series, obtained from 6-halogeno-4-ethylthioindoxyl by oxidation or condensation with a reactive 2-derivative of the corresponding 4-methyl compound, give bright yellowish-red shades.[76] A series of dyestuffs giving valuable subdued shades has been prepared from chloroalkoxymethylthioindoxyls condensed with reactive

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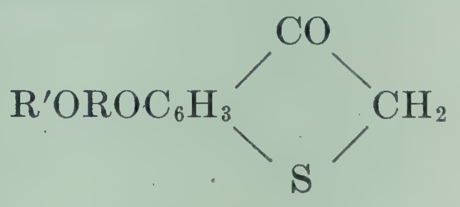
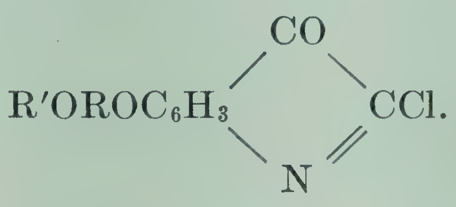
[75] du Pont, USP 2,158,032.

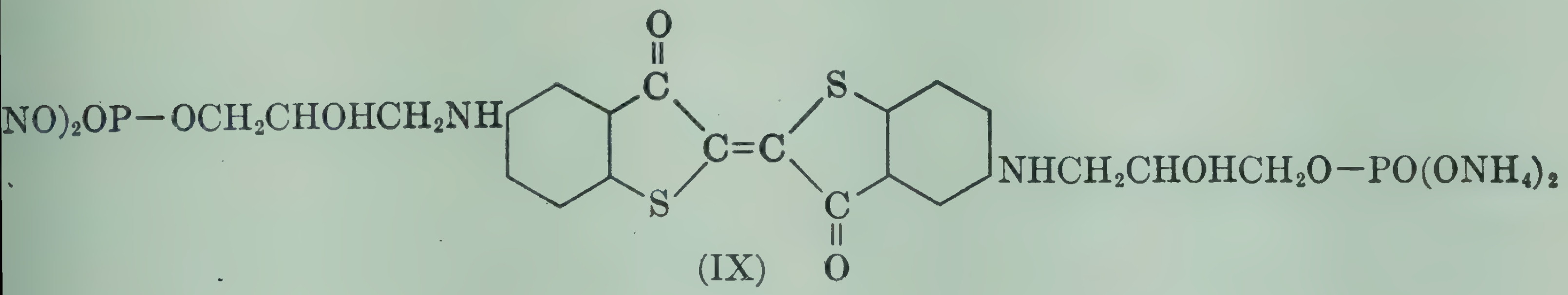
[76] IG, BP 442,167.

2-derivatives of thioindoxyl,[77] while dyestuffs having excellent covering power and light fastness have been prepared by condensing a dihalogenoalkylthioindoxyl with the usual components for indigoid dyestuffs; a monohalogenothioindoxyl may be used and the dyestuffs produced after-treated with a halogenating agent. 5,8-Dichloro-1,2-naphththioindoxyl, condensed with the *p*-dimethylaminoanils of thionaphthenequinones and other suitable components, gives a series of brown, gray, bordeaux-red and navy-blue dyes.[78] The preparation of fluorine-containing thioindigoid dyestuffs from fluorothioindoxyls either by oxidation or by condensation with an appropriate component has been described.[79] A number of alkoxyalkoxythioindigos and thionaphthene-indole-indigos have been prepared from thioindoxyls and reactive isatin derivatives of the general formulas





The dyes are characterized by their good solubility in organic solvents so that they may be used for dyeing acetate silk and coloring lacquers.[61] A series of indigoid and thioindigoid dyes (e.g. IX), suitable for dyeing cellulose acetate, have been described.[45]



(IX)

6-Chloro-5-methylthioindoxyl, made from 2-chlorotoluene-4-sulfonyl chloride, is condensed with an isatin or thioisatin, or their α-anils, for violet and brown dyes.[80] 6,7-Phthaloylthioindoxyl is oxidized to a brown, or condensed with an isatin α-chloride or a thioisatin-α-anil for gray, olive, or brown dyes.[81] Thioindigo-7,7′-dicarboxylic acid and its 4,4′-dichloro derivative are synthesized from the dichlorides of 2-carboxyarylthioglycolic acids,[82] and thioindigo or thionaphthene-indole-indigo residues united through a carboxyl group to one or two aminoanthraquinone residues provide a range of orange to black dyes.[83] When an 8-halogeno-1,2-naphththioindoxyl is condensed with a reactive 2′-derivative of a 2,1-naphththioindoxyl or vice versa, the dyestuffs give blackish brown shades, which are otherwise obtainable only with a mixture of vat dyes.[84]

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[77] IG, BP 442,185.

[78] Ciba, BP 467,447; 607,608; USP 2,453,225.

[79] IG, FP 803,813; Cf. du Pont, USP 2,061,186; 2,061,200.

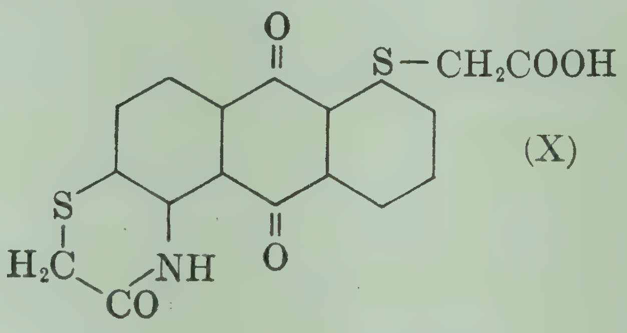
[80] Ciba, BP 372,640.

[81] IG, BP 361,406.

[82] IG, BP 360,349.

A new method for the synthesis of thioindigo derivatives, applicable to the naphthalene series, is to thionate α- or β-naphthyl methyl ketone with sulfur at 230–260°[85] or with sulfur chloride.[86] The α-compound gives a brown dye, identical with Indanthrene Brown RRD prepared by the cyclization of β-naphthylthioglycolic acid. Sulfur fusion of acetophenone gives only a trace of Thioindigo Red.[87] Sulfur fusion of 3-acetylpyrene yields *bis*-4,3-pyrenothiophene-indigo, a violet brown dye;[88] but IG, who have prepared the same dye by the normal method from the thioindoxyl derivative, state that it dyes cotton an intense blue shade.[89]

The device of introducing *o*-aminothioglycollic acid groups to give soluble dyes, capable of being made insoluble on the fiber,[90] has been applied in the thioindigo series: the intermediate (X) can be converted into a *bis*-anthraquinonethioindigo. The ketothiazine rings can be opened and the product applied as an acid dye and subsequently precipitated in the fiber. The dye from (X) gives a pure brown shade.[91]

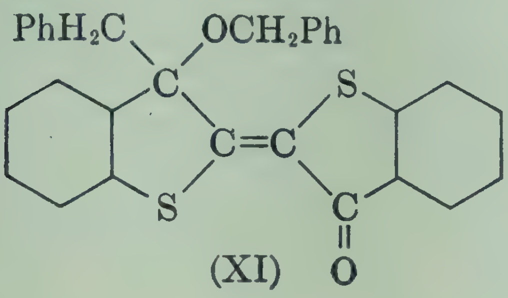


(X)

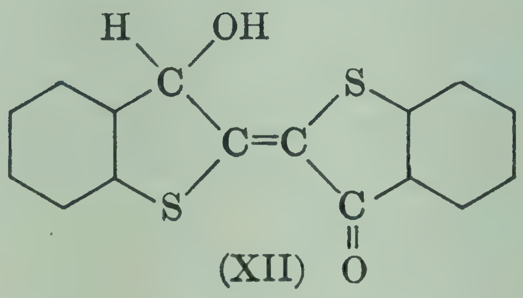
The leuco compounds of thioindigoid dyes present some problems which have not yet been solved.[92] Stable leuco derivatives of thioindigos, especially 6,6′-dichloro-4,4′-dimethylthioindigo and 2,1,2′,1′-naphththioindigo, can be prepared by reduction with alkaline hyposulfite.[93] IG have also noted that thioindigoid dyes substituted in the

[83] IG, BP 354,716.
[84] Ciba, BP 466,638.
[85] Dziewonski *et al.*, *Bull. acad. Polonais,* **A198** (1930).
[86] IG, BP 371,459.
[87] Jezierski, *Roczniki Chem.* **14,** 216 (1934).
[88] Dziewonski and Sternbach, *Roczniki Chem.* **17,** 101 (1937).
[89] BP 459,891.
[90] See Chapter XXIX.
[91] ICI, BP 398,161–2.
[92] Rodd and Piggott, *Annual Repts Chem. Soc. London* **18,** 99 (1933).
[93] du Pont, USP 2,136,427.

4 and 6 positions, when reduced with hyposulfite in the presence of a small quantity of alkali, give leuco compounds more stable to air than the "normal" leuco compound, and less soluble in alkali. The stable forms can also be produced by reduction in the presence of alcohol or catalytically.[94] These products are useful for printing pastes, especially when mixed with such solubilizing agents as benzylsulfanilic acid.[95] No explanation has yet been given of the difference between the stable and normal forms of these leuco compounds, but both appear to form the normal sulfuric esters with such reagents as chlorosulfonic acid.[96] Tschilikin,[97] by benzylating leucothioindigo, has obtained a dibenzyl derivative which from its reactions must have the structure (XI). He concludes that leucothioindigo is a mixture of (XII) and the normal leuco form;



(XI)

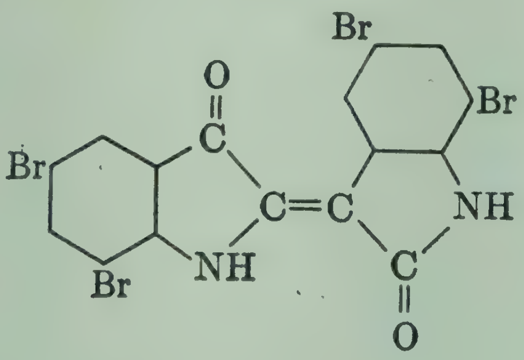


(XII)

but (XII) has not been identified with the "stable" leuco form of the patents.

2,3′-*bis*INDOLE-INDIGOS

Indirubin (CI 1204), an isomer of indigo and a minor constituent of natural indigo, has no commercial value. When it is applied by the usual hydrosulfite-alkali method, it appears to isomerize partly to indigo. Its occurrence in natural indigo is due to the partial oxidation of indoxyl to isatin; the condensation of indoxyl with isatin takes place unsymmetrically and therefore leads to indirubin instead of indigo. Brominating indirubin in hot nitrobenzene, the tetrabromo compound, Ciba Helio-



Ciba Heliotrope

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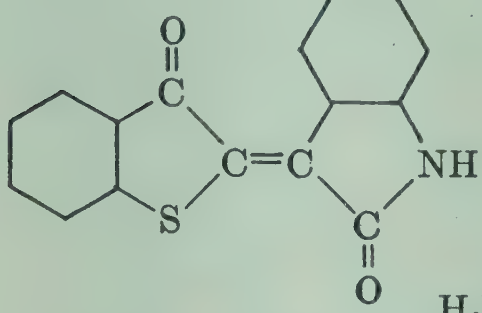
[94] IG, BP 334,878; 334,919; 338,104; 395,183.
[95] IG, BP 389,915.
[96] IG, FP 753,511.
[97] *Ber.* **65**, 1651 (1932).

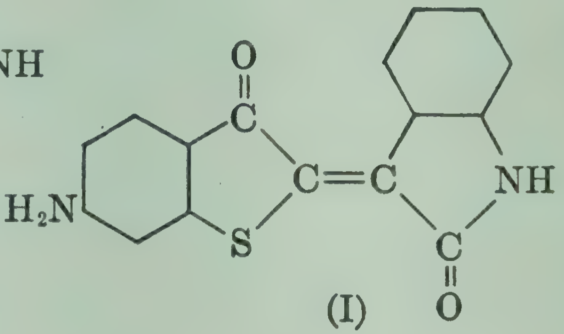
trope B (CI 1205), is a useful dye, although it has only moderate fastness. This dye can also be prepared by condensing 5,7-dibromoindoxyl with 5,7-dibromoisatin.

3-INDOLE-2′-THIONAPHTHENE-INDIGOS

Also called hemithioindirubines or the Thioindigo Scarlet class, some technically valuable dyes are found in this series. The condensation of isatin and thioindoxyl in sodium carbonate solution gives Thioindigo Scarlet R (Albrecht, 1905; CI 1225) (Durindone Scarlet R, ICI), which has moderate fastness and is useful in dyeing and calico printing. Replacing isatin in this reaction by its 5,7-dibromo derivative, the product is Thioindigo Scarlet G (Ciba Red G; CI 1226), which dyes a yellowish red. A new IG dye, not yet offered for sale, is Helindone Red FR, which has very good all-round fastness.[98] When 6-aminothioindoxyl is condensed with isatin and the product (I) is tribrominated, the dye Helindone Brown G (CI 1227) gives a moderately fast brown on cotton, wool and silk. Condensation of nitro- or aminoisatin with 6-aminothioindoxyl gives Algol Brown 5R (ST 1341), which has light fastness 4 and chlorine fastness 3–4.



Thioindigo Scarlet R



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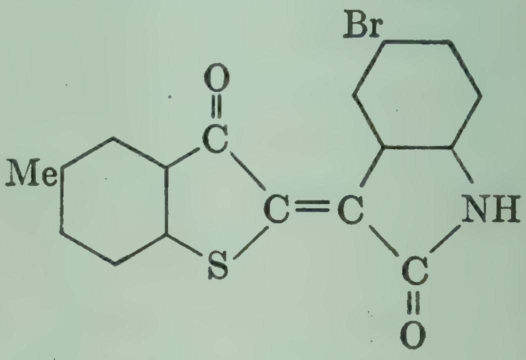
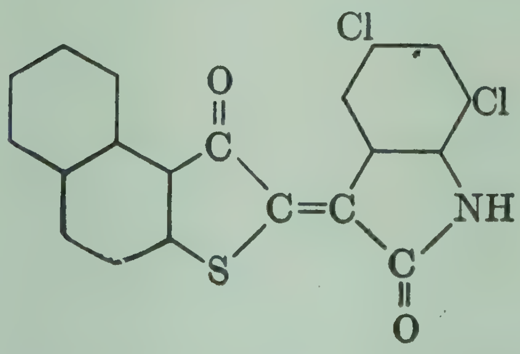
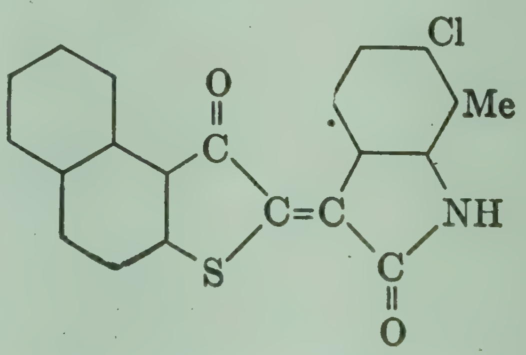


Helindone Red FR



Indanthrene Printing Brown R



Indanthrene Printing Brown 3R

Indanthrene Printing Brown R and 3R (IG, 1930) are prepared by the condensation of 4,5-benzothioindoxyl with the requisite isatin.[99]

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[98] *BIOS* Misc. Report **20.**

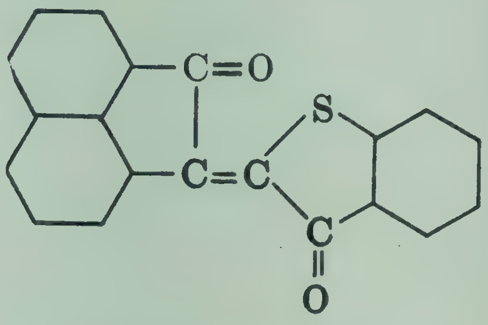
[99] Ref. 65 formulates both these dyes as 2,2′-derivatives.

Ciba[100] have described hemithioindirubins prepared by condensing 2,1-naphththioindoxyl or its derivatives with 6-bromo-7-methyl-isatin.

Miscellaneous Dyes from Indoxyl, Thioindoxyl, or Isatin

The last group among indigoid dyes, defined in the classification as dyes in which indoxyl, thioindoxyl or isatin is condensed with a suitable component, comprises a large number of dyes. This is understandable in view of the reactivity of indoxyl and thioindoxyl on the one hand towards carbonyl compounds, and of isatin, its chloride and anils on the other towards compounds containing a reactive methylene group.

The first important commercial dye (1907) of this class was Ciba Scarlet G (Grob, 1907; CI 1228) (Algol Scarlet GG; Helindone Scarlet GG) prepared by heating thioindoxyl and acenaphthenequinone in presence of sodium carbonate or caustic soda in dilute aqueous or alcoholic solution at about 90°; the dye is brightened by treatment with sodium hypochlorite (0.5–1% solution) at 90° for an hour.[65, 101] In addition to its being a fast and useful dye for cotton, wool and silk, the dye was of interest for its utilizing acenaphthene, a coal-tar hydrocarbon of no value at the time. Ciba Scarlet G is now prized for its outstanding brightness of shade, particularly suitable for printing. Monobromination in nitrobenzene solution occurs in the naphthalene half of the molecule and the product is Ciba Red R (CI 1229). By condensing 6-aminothioindoxyl with acenaphthenequinone and tribrominating, the product is Ciba Orange G (CI 1230), which dyes a bright pure shade of orange with good fastness properties.



Ciba Scarlet G

Friedländer found that indigoid dyes can be prepared by condensing isatin-2-chloride or 2-anil with naphthols and anthrols.[102] α-Naphthol gives two compounds in about equal amounts in this manner, and only one, in which the condensation takes place in the 2-position, has the indigoid structure possessing a $-\mathrm{CO}-\underset{|}{\mathrm{C}}=\underset{|}{\mathrm{C}}-\mathrm{CO}-$ chain. By condensing isatin chloride or anil with naphthols and anthrols, in which the condensation proceeds solely in the adjacent position, a series of vat dyes are obtainable. Thus the interaction of 4-bromo-1-naphthol, which may be assumed to function in the ketonic form (I), with 5,7-dibromoisatin chloride gives Alizarin Indigo 3R (Bauer and Herre, 1908; CI 1200) (Algol Blue 4R)[103] which dyes cotton a moderately fast reddish blue. An interesting property of the dye is that when it is applied in calico printing in conjunction with chromium acetate, a fast gray shade is obtained on steaming. Indanthrene Printing Blue GG (IG, 1930) is made by the condensation of 4-chloro-1-naphthol and 5-chloro-7-methoxy-4-methylisatin. The isatin is converted into the chloride by means of phosphorus trichloride and chlorine in chlorobenzene solution, the naphthol is added at 60°, and the reaction is complete in a few minutes. Indanthrene Printing Blue R is the product of the condensation of 1-chloro-4-naphthol with 5,7-dichloro-4,6-dimethylisatin.[59] A mixture of the dyes prepared by condensation of 4-halogeno- or 4,5-dihalogeno-7-alkoxyisatin with a naphthol or chloro- or bromonaphthol, either as such or by condensation of a mixture of components, is found to have increased color strength and tone as compared with the constituent dyes.[104] Alizarin Indigo G (By; CI 1202) (Algol Blue G, IG), a blue dye fast to chlorine (3–4), but only moderately fast to light (4), is the α-anthrol analog of Alizarin Indigo 3R; its present use is for conversion into Indigosol AZG.[33] The halogen atoms in these dyes are useful for enhancing the fastness, and such dyes can be prepared by halogenating the parent dyes free from halogen.[105] Helindone Blue 3G (Algol Blue 3GN;

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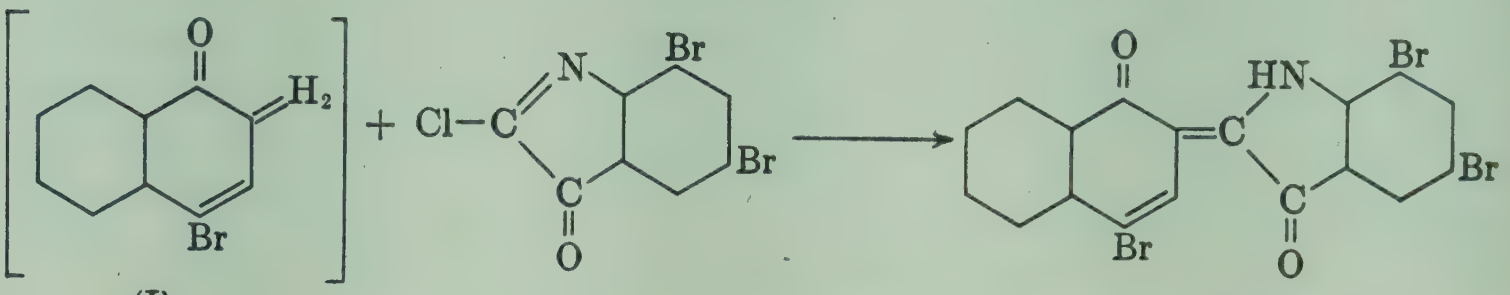
[100] Ciba, BP 541,097.

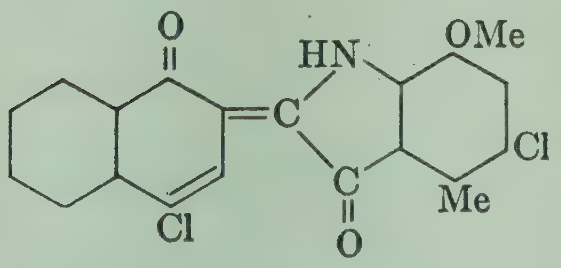
[101] Ciba, DRP 205,377; 210,813; 211,696; 226,244.

[102] *Ber.* **41,** 772 (1908).

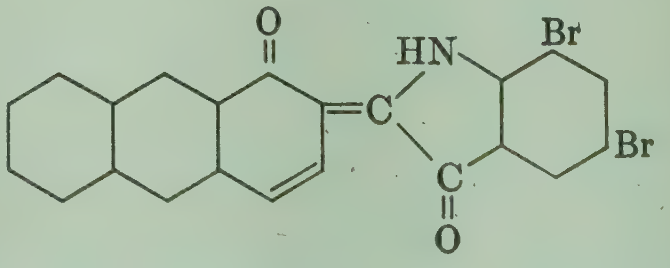


(I)

Alizarin Indigo 3R



Indanthrene Printing Blue GG



Alizarin Indigo G

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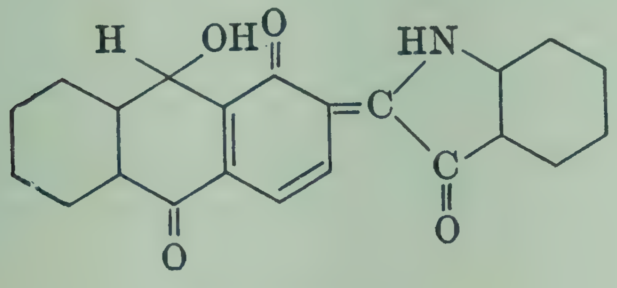
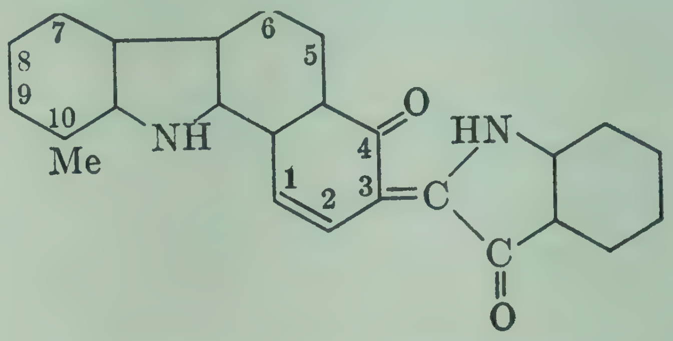
[103] Bayer, DRP 237,199.
[104] Ciba, BP 460,384.
[105] Ciba, BP 460,627.

ST 1331) is obtained by condensing isatin chloride with 1,9-dihydroxy-10-anthrone; it has poor fastness properties for a vat dye (light 4, chlorine 2–3). Algol Brilliant Green BK, the condensate of a chlorobromobenzoisatin with 4-methoxy-1-naphthol,[37] has low light fastness (3). Black dyes can be produced by the employment of carbazole derivatives, and an example is Indanthrene Printing Black B (IG), prepared by the condensation of isatin α-anil with 4-hydroxy-10-methyl-α-benzocarbazole in presence of acetic anhydride and formic acid at −8° to 45°.[53] It gives intense black shades, but has been largely replaced by Indanthrene Printing Black BL which has superior printing properties.


Algol Blue 3GN


Indanthrene Printing Black B

The number of indigoid dyes which can be prepared by using one or other of the various routes mentioned earlier, and by the combination of suitable intermediates of the benzene, naphthalene, acenaphthene, anthracene and heterocyclic series, is legion. The indigoid dyes are comparable to the azo dyes in the sense that the dyes are prepared by the interaction of two components, each of which is variable within wide limits. Since the condensations are relatively easy to carry out and dyes of unambiguous constitution result, many have been prepared and studied from the point of view of the relation between color and chemical constitution.[106] On the technical side Ciba have been particularly active in this field.

Dutta[107] has described a series of dyes obtained by condensing 1,2-, 2,1- and 2,3-naphthoxythiophenes (naphthioindoxyls) with *o*-diketones such as phenanthraquinone, acenaphthenequinone and isatin. The absorption curves of thirty-six such thioindigoid dyes in nitrobenzene were determined. All the 2,3-isomers absorb at longer wave lengths than the 1,2- and 2,1-compounds, and the intensities are also greater. The 1,2- and 2,1-compounds have very similar structures, as indicated by the similarity of their absorption curves. Dutta[107] has suggested that a 5-

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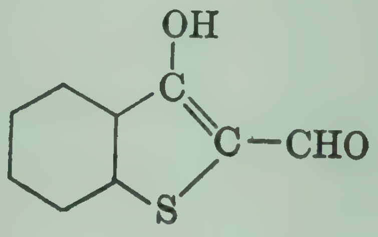
[106] Friedländer *et al., Ber.* **55,** 1591 (1922) and other papers; Pummerer *et al., Ber.* **64,** 831 (1931) and other papers; Guha, *J. Indian Chem. Soc.* **23,** 103 (1946) and earlier papers.

[107] *Ber.* **68,** 1447 (1935); **69,** 2343 (1936); and earlier papers.

or 6-membered ring may be formed by hydrogen-bonding between the sulfur or oxygen atom and the peri-hydrogen atom in the 1,2- and 2,1-derivatives of naphthalene, but such ring formation is not possible in the compounds derived from 2,3-naphththioindoxyls. The 2,3-compounds are deeper colored than the 1,2 and 2,1-isomers, because the postulated chelation weakens the chromophoric influence of the sulfur or carbonyl group.

DEGRADATION OF INDIGOID DYES

Many indigoid dyes, on heating with alkali, undergo hydrolytic fission into two components, identification of which establishes the constitution of the dye.[3] The *bis*indole-indigos and thionaphthene-indole-indigos give an anthranilic acid derivative, together with a 3-hydroxy-indole-2-aldehyde or the sulfur analog (I). 2-Naphthalene-2′-indole-indigo gives 1-naphthol-2-aldehyde. Thioindigo, in line with its greater stability to all reagents in comparison with indigo, is more resistant to alkali fusion. With alcoholic potassium hydroxide, thioindigo breaks up to thioindoxyl, thionaphthenequinone and the thioindogenide of 3-hydroxythionaphthene-2-aldehyde; but many substituted thioindigos do not undergo such fission. The action of ozone on thioindigoid dyes results in the formation of the corresponding thionaphthenequinones. Oxidation of thioindigo with fuming nitric acid gives *o*-sulfobenzoic acid. Raney nickel reduction of thioindigoid dyes leads to the corresponding diphenacyls and diphenylbutanes, which on oxidation under pressure with 5% nitric acid yield substituted benzoic acids.[107a]



(I)

APPLICATION OF INDIGOID DYES

The indigoids give pale yellow or pale brown vats in contrast to the deep colors of the anthraquinone vats. Older methods of vatting indigo (fermentation, glucose and alkali, zinc-lime, ferrous sulfate) have been superseded by the hydrosulfite-alkali method now used for all vat colors with suitable variations in the quantities of the reagents and temperature of vatting. The slightly higher cost of the hydrosulfite-caustic soda vat is more than offset by the advantage of saving in the dyestuff, clarity of the dyebath and faster dyeings. The fermentation vat, however, is still used for special purposes, such as the dyeing of heavily milled woollen fabrics in which better penetration is obtained by this method. Among the various processes for the preparation of the vats, the stock vat process is preferred. Control of the alkalinity during dyeing is essential; with a deficiency in alkali the penetration is poor, the shades are redder, and the fastness to rubbing is inferior; with excess alkali the shades are apt to be unlevel, and the wool fiber will be damaged. For wool dyeing ammonia may partially replace caustic soda. Fastness to rubbing requires careful attention in indigo dyeing, and it is only in the hands of an expert and experienced dyer that indigo shades have satisfactory rubbing fastness. Because of the lower substantivity of leucoindigo in comparison with the leuco derivatives of halogenated indigos, the thioindigoids and the anthraquinonoid vat colors, indigo dyeing has usually to be carried out by a building-up process, in which the goods are dipped in the dye liquor several times with an intermediate air-hanging for yarn or overhead run for piece-goods for oxidizing the vat after each dip. As stated earlier, indigo has much better fastness on wool than on cotton and is much more extensively employed for the animal fiber.

[107a] Pummerer and Luther, *Ber.* **64,** 831 (1931); Fürst and Pollak, *ibid.* **65,** 390 (1932); Reisz, *ibid.* **64,** 1893 (1931); Kao, Tilak and Venkataraman, *Proc. Indian Acad. Sci.* **32A,** 162 (1950).

Indigo derivatives and thioindigoid dyes are applied by the general methods of vat dyeing.[108] Here again, these dyes are more useful for wool than for cotton, but in calico printing the indigoids are largely used. When wool is dyed with vat dyes from weakly alkaline vats, protective colloids such as glue or casein are often added, and full shades with good fastness to rubbing are difficult to obtain. A method suggested for producing a full shade is to dye a weaker shade with the vat dye first and then cross-dye with an acid color. The acid dye may be applied first and the vat dye in a subsequent operation.[109]

The indigoids in the form of the solubilized dyes (Indigosols) are used for both dyeing and printing of cotton fabrics.[33] In their fastness properties on cotton, the indigoids as a class are inferior to the anthraquinone vat dyes, especially in fastness to light, although there are individual exceptions.

Indigoid dyes can be applied to cellulose acetate fabrics by padding successively with an aqueous suspension of the dye and an aqueous solution of formaldehyde-sulfoxylate made alkaline with an alkanolamine, followed by steaming to effect vatting. Saponification of the acetate does not take place materially under these conditions.[110]

[108] See Chapters VI and XXX.

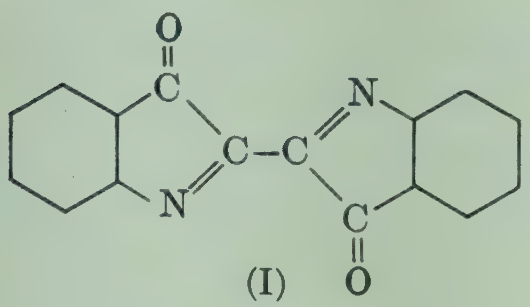
[109] Weber and Allied Chemical and Dyestuff, USP 2,420,729.

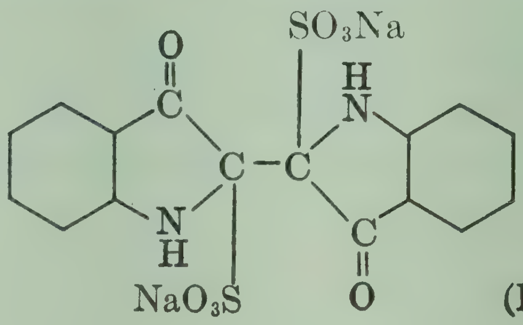
[110] British Celanese, BP 635,310.

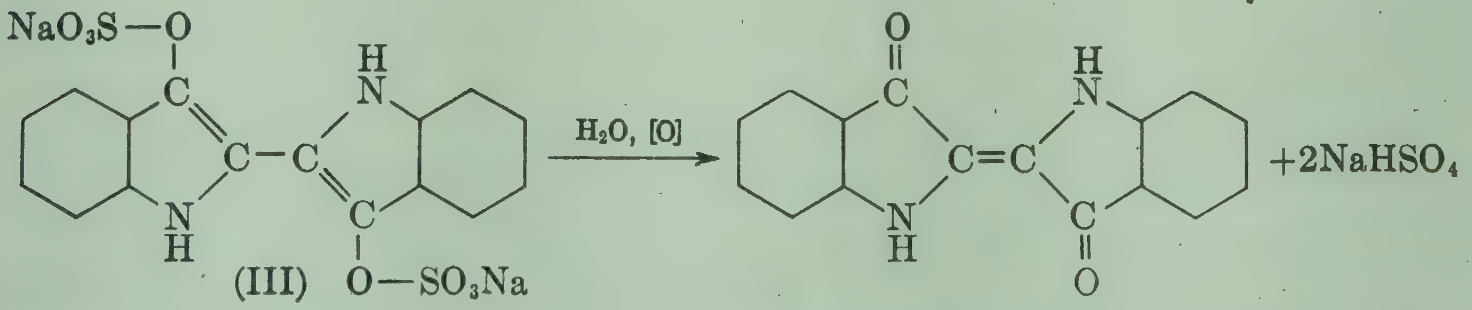
Chapter XXXIV

SOLUBILIZED VAT DYES

In the course of a search for a method of applying indigo to wool by a process not involving alkali, Kalb oxidized indigo to dehydroindigo (I), which gave a water-soluble bisulfite compound (II). When wool or cotton was steeped in this solution, dried and passed through hot acid or alkali, the material was dyed blue, but only half the indigo was regenerated and the method was not a commercial success. Attempts were then made to make water-soluble esters of leucoindigo, and the problem was solved in 1921 by Bader and Sunder who succeeded in preparing a disulfuric ester from which indigo could be regenerated readily and quantitatively.[1] Dry leucoindigo, prepared by precipitating the alkaline vat with carbon dioxide and drying in absence of air, was added in an atmosphere of carbon dioxide to the addition compound of pyridine (or dimethylaniline) and chlorosulfonic acid obtained by dropping the acid into the base with cooling and stirring. The mixture was stirred cold, warmed to 50–60°, diluted with hot water, and cooled, when the pyridine salt of the disulfuric ester of leucoindigo crystallized in 80–90% yield. On adding caustic soda to an aqueous solution, the sodium salt (III) separated. The substance, which crystallizes with $10H_2O$, was marketed


(I)


(II)


(III)

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[1] Durand and Huguenin, BP 186,057; USP 1,448,251.

as Indigosol O (DH). It is an isomeride of Kalb's dehydroindigobisulfite compound, but unlike the latter it regenerates indigotin quantitatively and instantaneously on treatment with suitable oxidizing agents. The aqueous solution is slowly affected by air oxidation.

Although Indigosol O is decomposed by acids, in presence of wool it is unaffected even by boiling acids, and it can be applied to wool as an acid dye from a bath containing sodium sulfate, acetic acid and formic acid. The soluble dye is substantively absorbed by the fiber, which is then treated with dilute sulfuric acid and an oxidizing agent such as sodium nitrite, dichromate or ferric chloride to effect the development of the color.

Cotton is impregnated with an aqueous solution of Indigosol O, dried, and the color developed in a bath containing ferric chloride and hydrochloric acid, or sodium nitrite and sulfuric acid. Drying after impregnation is necessary for this Indigosol, which has practically no affinity for cellulose. According to the concentration of the impregnation bath, any depth of shade can be produced in one operation, whereas a deep shade of indigo is obtained ordinarily by a somewhat tedious building-up process. By using Indigosol O a dyeing as fast as a vat dyeing is obtained, but penetration of the fiber and fastness to rubbing are improved.

The reaction $[-CO- \rightarrow -C(OH)= \rightarrow -C(O-SO_3Na)=]$ for the preparation of these sulfuric ester salts of the leuco compounds can in principle be applied to all vat dyes. Indigosols derived from several indigoid dyes were prepared by DH, and Indigosol 04B (Soledon Blue 4BCS) from tetrabromoindigo was especially important because of its affinity for cotton, the attractive shade and its good fastness properties; but difficulties were encountered in applying the original Bader-Sunder process to a wider range of vat dyes, particularly the anthraquinonoids. The preparation of the leuco derivative of the vat dye in solid form, prior to sulfation, was not possible with many vat dyes; the leuco derivatives were either too soluble for separation after alkaline reduction of the vat dyes, or did not possess adequate stability for this purpose. A notable advance in the method of preparation of such solubilized vat dyes, which can be applied with equal success to anthraquinonoid and indigoid vat dyes, was then made by Morton Sundour Fabrics.[2] The method is based on the discovery that when a vat dye is treated with fuming sulfuric acid (or an alkyl ester of chlorosulfonic acid, or a mixture of chlorosulfonic acid and phthalimide), a metal (copper, zinc, iron) and pyridine (or other tertiary base), a metal complex (IV) of the pyridine salt of the leuco derivative of the dye is formed. An important feature of the reaction is that the complex (IV) is formed directly from the vat dye without

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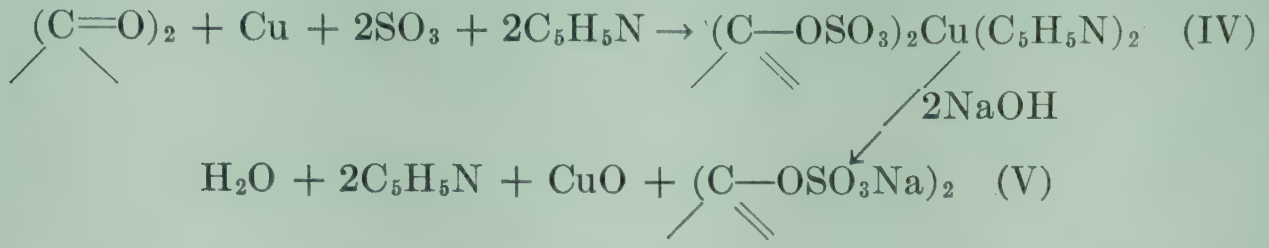
[2] Jones, Wylam, Morton, and Morton Sundour Fabrics, BP 245,587; 248,802; 251,491; Thomas, Harris, Wylam, and Scottish Dyes, BP 258,626; Scottish Dyes, BP 334,902; IG, BP 461,430; Fairweather and ICI, BP 630,459.



$$(\mathrm{C{=}O})_2 + \mathrm{Cu} + 2\mathrm{SO_3} + 2\mathrm{C_5H_5N} \rightarrow (\mathrm{C{-}OSO_3})_2\mathrm{Cu}(\mathrm{C_5H_5N})_2 \quad \mathrm{(IV)}$$

$$\xrightarrow{2\mathrm{NaOH}} \mathrm{H_2O} + 2\mathrm{C_5H_5N} + \mathrm{CuO} + (\mathrm{C{-}OSO_3Na})_2 \quad \mathrm{(V)}$$

the intermediate formation of the leuco compound as in the Bader-Sunder method, since completely anhydrous reactants are used and no source of hydrogen is available. The procedure may be varied by suspending a vat dye in pyridine, and treating with a metal and a sulfating agent or source of sulfur trioxide. The complex (IV) is finally converted into the sodium salt (V). ICI market their solubilized vat colors under the name of Soledons. While the anthraquinone vat colors were usually not amenable to conversion to the sulfuric esters by the Bader-Sunder method, so that the earlier Indigosols were mainly indigoids and thioindigoids, most of the Soledons are derived from anthraquinone vat dyes (e.g., Soledon Blue 2RC, Dark Blue 2R, Jade Green X, Yellow G, Orange 4R, Brilliant Purple 2R and Black 2B).

Solubilized vat colors derived from indanthrone can be conveniently prepared by careful oxidation of the disulfuric ester of the leuco compound of the appropriate β-aminoanthraquinone derivative under alkaline conditions.[3] An example is Indigosol Blue IBC (Soledon Blue 2RCS), a tetraester which cannot be made directly from dichloroindanthrone by either the DH or ICI method, since a much less soluble diester is thus obtained. These tetraesters can be submitted to acid oxidation for the preparation of indanthrone and its derivatives in substance in very pure form.[4] Indigosol Blue IBC is prepared from 2-chloro-3-aminoanthraquinone by the indicated reactions.[5, 6] If a halogen is present in the 1-position, it is eliminated during the conversion of the 2-acetamidoanthraquinone into the sulfuric ester of the anthrahydroquinone; and there are advantages in starting for instance from 1,3-dibromo-2-aminoanthraquinone.[7] The conversion of 2-chloro-3-acetamidoanthraquinone to the leuco sulfuric ester can be carried out in two stages: (a) reduction to the leuco derivative by treating a solution in chlorobenzene, dimethylaniline and pyridine with hydrogen at 60–65° and 19 atms. pressure in presence of a nickel catalyst; and (b) esterification with

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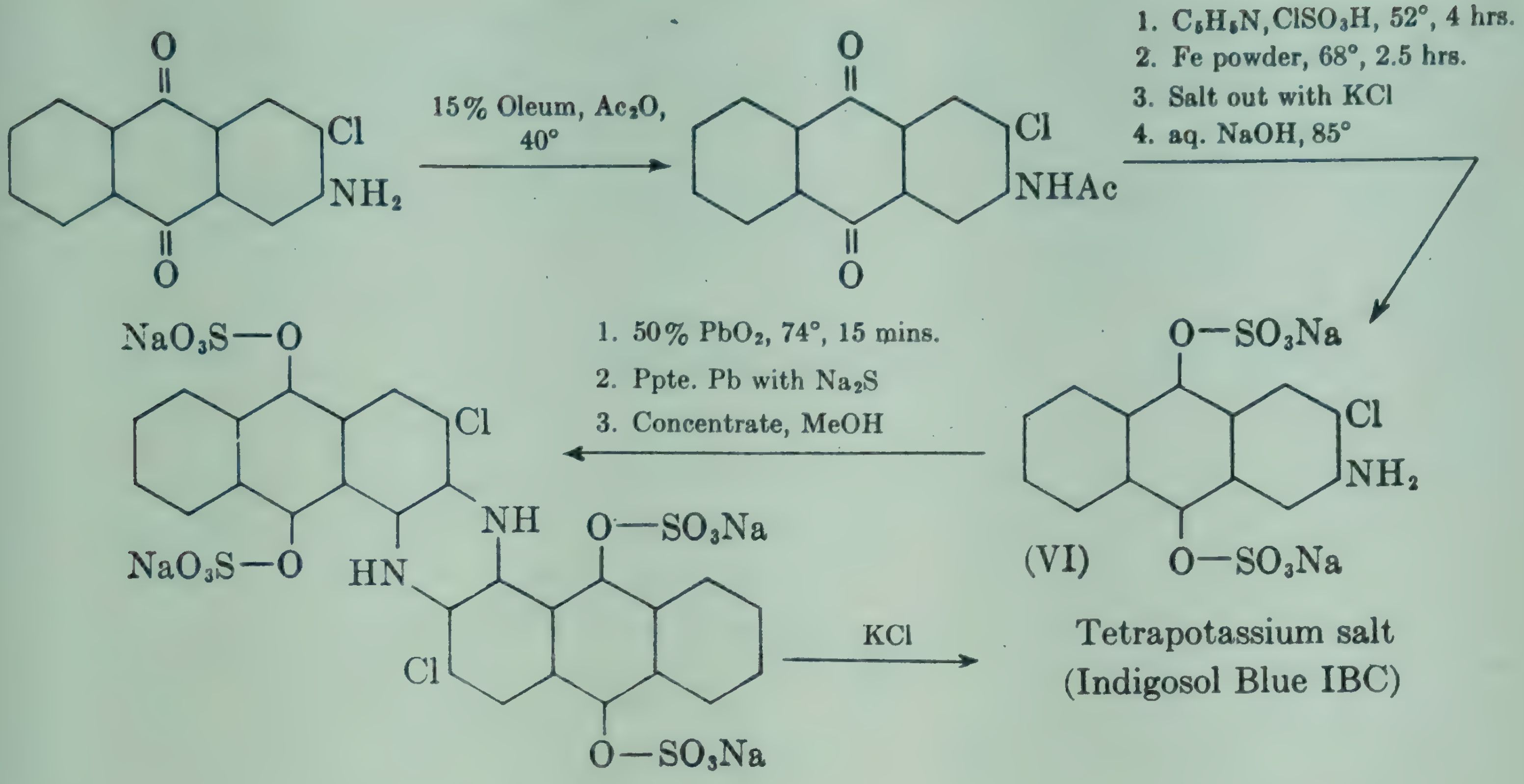
[3] IG, BP 416,939.

[4] IG, DRP 470,809; 574,190. See also Bretagne, USP 2,344,389.

[5] *BIOS* **960**; **1363**; *FIAT* **1313**, II.

[6] *BIOS* **1493**.

[7] Stallmann and du Pont, USP 2,200,480.



chlorosulfonic acid in dimethylaniline and chlorobenzene.[6] Lead peroxide may be replaced by silver oxide[8] or the oxidation of (VI) to the Indigosol may be effected electrolytically.[9]

Details of the current IG methods of preparation of the solubilized vat colors are now available.[5] The name Anthrasol replaces the old Indigosol, apparently as a result of the cessation of the agreement with the Swiss firm of DH; but the name Indigosol is retained here, since the available shade cards refer to the Indigosols and DH continue to market them under the old names. With the exception of Indigosols 0 and 04B which are still made by the earlier process of treating the leuco dye with chlorosulfonic acid and dimethylaniline, all the Indigosols are now made by the ICI pyridine-metal method, which IG claim to have improved in certain details. Pure pyridine is used for Indigosol Red IFBB, Brown IBR, and Green I3G; and a mixture of α- and γ-picolines for all other Indigosols. The metal generally used for the complex formation is electrolytic iron; exceptions are Red IFBB for which copper is used, since iron gives lower yields and duller shades, and Blue IBC and Green I3G for which iron in the cheaper form of needle dust is adequate. The vat dyes are used in finely powdered form, unless the reaction mass becomes too thick as a result. Esterification is carried out in an iron reaction kettle (enamelled for Red IFBB), provided with an anchor type agitator. The general procedure is to treat pyridine with chlorosulfonic acid, maintaining the temperature at 20°. The vat dye and iron are added simultaneously, or the dye is added first. The reaction temperature is about 60°, and may be allowed to rise up to 80°; the temperature must be kept at 40° for Red IFBB. The time of reaction varies, some being rapid and others taking several hours. The progress of the reaction is followed by the appearance of the mixture and the solubility in water. The yields are between 80 and 90%. The usual method of isolation of the Indigosol is to blow the reaction mixture by means of nitrogen into sodium carbonate solution, add a little rapeseed oil to control frothing, and distil with indirect steam. The distillate is 30–40% pyridine, and the distillation is continued until the residual liquor does not liberate pyridine on the addition of caustic alkali. Iron and iron oxide (together with kieselguhr which may be added for clarification and as a filter aid) are filtered off in a wooden filter press, and the Indigosol is salted out from the filtrate, after prior concentration in vacuum if the Indigosol is too soluble (e.g., Brown IBR, Blue IBC and Indigosol O). The precipitated Indigosol is filtered off on a cloth-covered iron nutsch. Soda ash and urea as stabilizers (together sometimes with dimethylaniline sulfonic acid for improving the solubility) are added to the Indigosol, which is then homogenized. The addition of dimethylaniline sulfonic acid may also be made at the standardization stage. The paste is finally dried in a vacuum shelf dryer at 50–60°. Standardization is mainly with sodium sulfate, but common salt can also be used. Very insoluble Indigosols (e.g., Brilliant Orange IRK, which is only marketed in paste form) may be pasted with triethanolamine. Blue IBC is marketed as paste and powder, and the others are in powder form. The Indigosols in general are stable during isolation, drying and storage. Indigosol Red IFBB is not stable to long storage, probably because copper is used in its preparation. Blue IBC has a tendency to revert to the parent vat dye.

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[8] Kuhlmann, BP 577,167.

[9] IG, FP 779,890.

Recovery of pyridine and its reuse, after concentration and drying by azeotropic distillation with benzene, substantially influence the economy of the process. The overall loss of pyridine is 15% in summer and 7% in winter. Attempts to replace pyridine by cheaper tertiary bases have so far been unsuccessful.

About 35 Indigosols and 25 Soledons have been marketed. Their names and those of the parent dyes are listed in Table I.[5] For simplicity only one name (usually IG) for the parent vat color is stated. The identity of the vat dyes corresponding to the Soledons has been indicated on the basis of the shades and color reactions.[10] The parent vat colors (VII), (VIII), (IX), (X) and (XI)[5, 11, 11a] are produced specifically for conversion into the Indigosols and are not marketed as vat dyes. The

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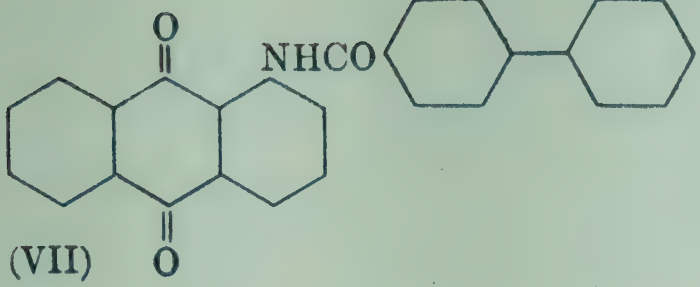
[10] Cf. Fox, Vat Dyestuffs and Dyeing, Chapman and Hall, London, 1946.

[11] *BIOS Misc. Report* **20.**

[11a] See also Durand and Huguenin, BP 607,219; USP 2,388,285.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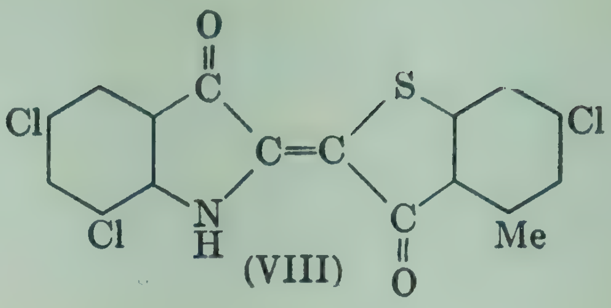
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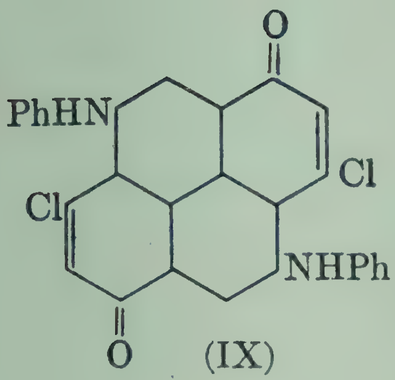
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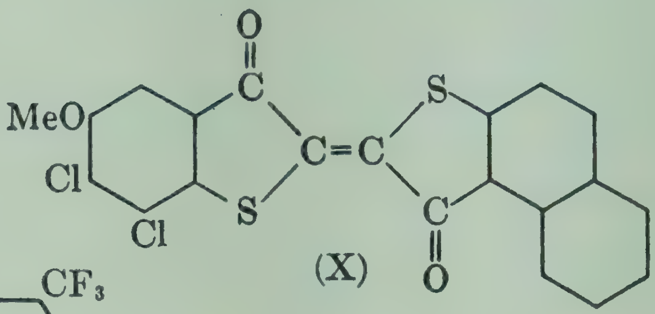
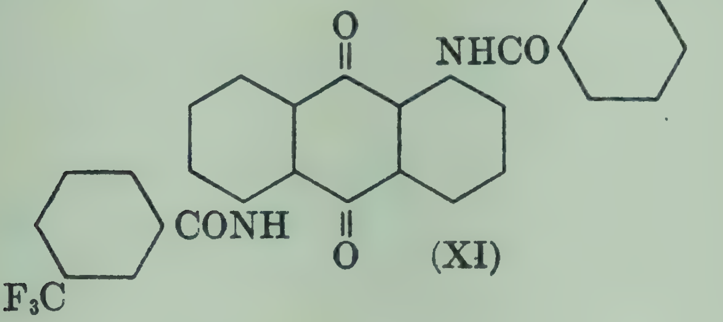
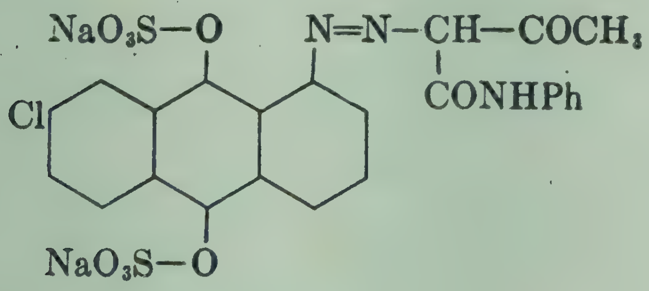

(X)


(XI)

parent vat dye for Anthrasol Brown IVD has also been stated to be an isomer of (X) in which one of the chlorine atoms is in the naphthalene ring.

Anthrasol Printing Yellow IG and I3G are azo dyes, and they have not yet been offered for sale.[11] Yellow I3G is similar to Yellow IG, and is made from the azoic dye (α-Aminoanthraquinone → Acetoacet-*p*-chloroanilide). The bright yellow shades have good fastness properties and are of special interest in calico printing. Dyestuffs having the combined characteristics of azoic dyes and of sulfuric esters of reduced vat dyes were at one time marketed under the name of Solazols (e.g., Solazol Red 2B) (ICI). They were made by diazotizing the sulfuric esters of leuco vat dyes containing a primary amino group and coupling with


Anthrasol Printing Yellow IG

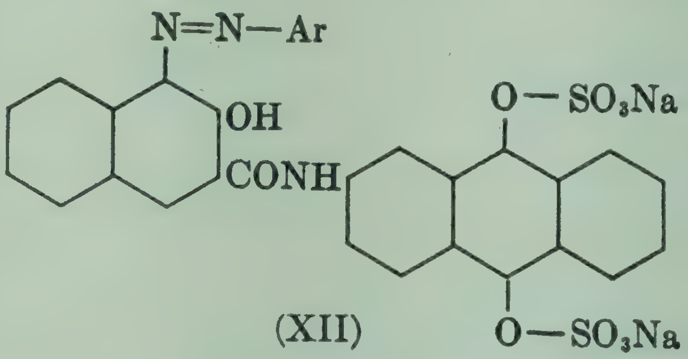

(XII)

TABLE I

Indigosol; Anthrasol	*Soledon*	*Parent vat dye*
1. Yellow HCG	—	Helindone Yellow CG
2. Yellow I2G	—	(XI)
3. Golden Yellow IGK	Golden Yellow GKS	Indanthrene Golden Yellow GK
4. Golden Yellow IRK	Golden Yellow RKS	Indanthrene Golden Yellow RK
5. —	Yellow GS	Indanthrene Yellow G
6. Yellow V	—	(VII)
7. —	Yellow 5GS	Caledon Yellow 5GS
8. Orange HR	Orange RS	Algol Orange RF
9. —	Orange 4RS	Indanthrene Orange 4R
10. Brilliant Orange IRK	Brilliant Orange 6RS	Indanthrene Brilliant Orange RK
11. Pink IR extra	Pink FFS	Indanthrene Brilliant Pink R
12. Brilliant Pink I3B	—	Indanthrene Brilliant Pink 3B
13. Red IFBB	Red 2BS	Indanthrene Red FBB
14. Red Violet IRH	Red 3BS	Indanthrene Red Violet RH
15. Red HR	—	Algol Red BB
16. —	Scarlet BS	Durindone Scarlet 3BS
17. Scarlet HB (mixture of Anthrasol Orange HR and Anthrasol Pink IR extra)	—	—
18. Scarlet IB	—	Indanthrene Scarlet B
19. Brown IRRD	Brown GS	Indanthrene Brown RRD
20. Brown IBR	Dark Brown 3RS	Indanthrene Brown BR
21. Brown IVD	Red Brown BS	(X)
22. —	Brilliant Purple 2RS	Indanthrene Brilliant Violet 2R
23. Printing Violet IBBF (Violet ABBF)	Violet BS	Indanthrene Printing Violet BBF
24. Printing Purple IR (Purple AR)	—	Indanthrene Printing Purple R
25. Brilliant Violet I4R	—	Indanthrene Brilliant Violet 4R
25a. Brilliant Violet I4B	—	Indanthrene Brilliant Violet 3B
26. Printing Violet IRR (Violet ARR)	—	(VIII)
27. O	Indigo LL	Indigo
28. OR	—	Monobromoindigo
29. 04B	Blue 4BCS	Tetrabromoindigo
30. (Blue) 06B	—	Hexabromoindigo + pentabromoindigo
31. 04G	—	Brilliant Indigo 4G
32. AZG	—	Algol Blue G
33. Printing Blue IB	—	Indanthrene Printing Blue B
34. Printing Blue IGG (Blue AGG)	—	Indanthrene Printing Blue GG
35. Blue HB	—	Algol Blue B
36. —	Blue 4GS	—
37. Blue IBC	Blue 2RCS	Caledon Blue RC
38. Blue IGC	—	Indanthrene Blue GC
39. —	Dark Blue 2RS	Indanthrene Dark Blue BO

TABLE I (*Continued*)

Indigosol; Anthrasol	*Soledon*	*Parent vat dye*
40. Green I3G	Brilliant Green 5GS	(IX)
41. Olive Green IB	Green GS	Indanthrene Olive Green B
42. Green AB	—	Algol Brilliant Green BK
43. Green IB (IBA)	Jade Green XS	Caledon Jade Green X
44. Green IE3B	Jade Green 3BS	Caledon Jade Green 3B
45. Green IGG	Jade Green 2GS	Caledon Jade Green 2GS
46. Gray IBL	Gray BS	Indanthrene Printing Black BL
46a. Gray IN	—	Indanthrene Olive T
47. Blue Black IRD	—	Indanthrene Printing Black BGL
48. Printing Black IB	—	Indanthrene Printing Black B
49. —	Black 2B	—

arylamides of hydroxynaphthoic acid.[12] A recent suggestion is to prepare (XII) by benzoylating the β-anthraquinonylamide of hydroxynaphthoic acid, converting it into the sulfuric ester of the leuco derivative, debenzoylating by alcoholic alkali, and coupling with a diazonium salt (Ar free from solubilizing groups).[13]

Various modifications in the preparation of the sulfuric esters of leuco vat dyes have been suggested in the patent literature. Sulfation by means of the sulfur trioxide compounds of tertiary amines having a dissociation constant of at least 1×10^{-7} (e.g., *N*-ethylmorpholine or trimethylamine) may be carried out in aqueous alkaline media.[14] For 1,4-bisbenzamidoanthraquinone, a mixture of cuprous chloride, brass powder and the vat dye is added to a suspension of sodium pyrosulfate in pyridine.[15] Vat dyes and anthraquinone intermediates are converted into their leuco sulfuric esters by reduction with a metal in presence of dimethylformamide or methylamine, followed by sulfation with the addition compound of sulfur trioxide and dimethylformamide.[15a] A stable leuco compound (e.g., of 16,17-dihydroxydibenzanthrone) is obtained as the monosodium salt from a hydrosulfite vat by reducing the pH to 9–12 at 60–90° until precipitation is complete; this compound forms a blue solution in sulfuric acid, and is unchanged on precipitation, even after heating at 100°; it can be converted into the disulfuric ester in the normal way.[16] The β-hydroxyethyl and homologous ethers are obtained from the stable leuco compound of 16,17-dimethoxydibenzanthrone and its *iso* analog; their acid sulfates dye cotton red, regenerated to the parent shades by acid.[17] Very fast, brilliant reds are produced by the leuco sulfuric esters prepared from 1,4-bis-acylamidoanthraquinones in which at least one of the acids is a diarylsulfone carboxylic acid.[18] The addition of urea and a sulfobetaine containing an aralkyl radical is useful in dyeing cotton and viscose rayon with Indigosols.[19] The stability of the Indigosols from the benzanthrone dyes is increased by the addition of salts of mercaptans such as dithiocarbamic acid or mercaptobenzothiazole.[20] The triethanolamine salts of the sulfuric esters have improved printing qualities.[21] Cellulose acetate fabrics can be dyed uniform shades by impregnation with the dyes in a 70% aqueous solution of lower aliphatic alcohols or ketones.[22]

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[12] BP 333,506–7; USP 2,316,758.

[13] Marschalk and Kienzle, *Teintex* **12,** 75 (1947).

[14] Lecher, Scalera, and Lester, BP 585,106; USP 2,396,582; 2,402,647; 2,403,226; Lecher and Hardy, *JACS* **70,** 3789 (1948). The reaction proceeds smoothly with indigoids and with anthrone derivatives, but with anthraquinone derivatives disproportionation to anthraquinone and anthranol derivatives occurs; Scalera *et al.*, *JACS* **73,** 3094 (1951).

[15] Coffey, Driver, Fairweather and ICI, BP 605,617; USP 2,504,806.

[15a] Coffey *et al.* and ICI, BP 610,117; 633,480–1; 633,483–7; 633,501–2; 633,504–5; 633,492–3; 633,498–9; 633,513.

[16] USP 2,148,042; USP 2,188,320.

Vat colors solubilized in forms other than the leuco-sulfuric esters have been mentioned. If leucoindigo is condensed with chloroacetic or β-chloropropionic acid, the product is oxidizable on the fiber to the parent dye by means of oxidizing agents such as ferric chloride.[23] Acylation may be effected with benzoic acid-*m*-sulfonyl chloride,[24] and both these types of products are specially recommended for printing. The vat dye (e.g., 16,17-dimethoxydibenzanthrone) is heated with copper, pyridine, and an organic acylating agent having in addition to the acylating group at least one salt-forming group or group convertible into quaternary ammonium (e.g. *p*-chloromethylbenzoyl chloride).[25] The products are more stable to acids and less stable to alkalis than the sulfuric esters. The aqueous vat (e.g. of dibenzanthrone) is treated at about 5° with *o*-sulfobenzoic anhydride in presence of a condensation product of *n*-octadecyl alcohol (1 mole) and formaldehyde (20 moles); the leuco-ester is then salted out.[26] Esters of the stable leuco compounds mentioned earlier with fatty acids of not less than eight carbon atoms, especially the dilaurates, are useful oil-soluble fluorescent colors.[27] The quaternary salt of carbylsulfate and pyridine is used as the esterifying agent, which is heated with the pure dry leuco derivative of the vat dye, or with the pure vat dye and copper powder.[28]

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[17] Stallmann and du Pont, USP 2,183,626–7; 2,183,629–30.

[18] Kern and Ciba, USP 2,439,626.

[19] Ratti, Brandt, and Durand and Huguenin, USP 2,437,554.

[20] IG, BP 452,018.

[21] du Pont, USP 1,954,702.

[22] Croft, Hindle, and Celanese Corporation of America, USP 2,428,833.

[23] Ciba, BP 291,768.

[24] IG, BP 324,119; 497,327.

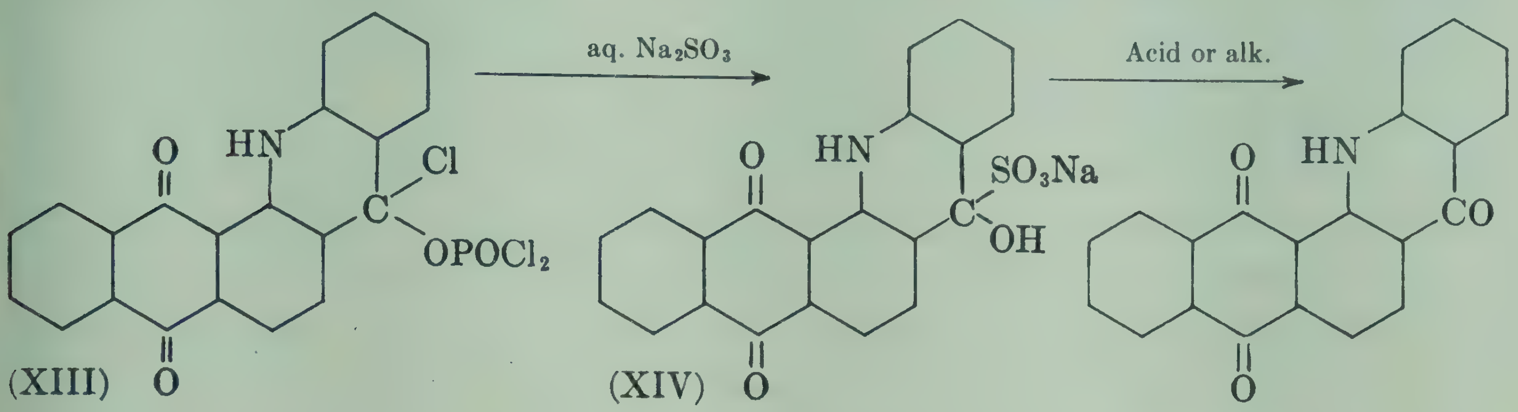
[25] IG, BP 497,327.

[26] Mieg, Wieners, and General Aniline and Film, USP 2,307,893.

[27] Stallmann and du Pont, USP 2,183,628.

[28] Stallmann, Prahl and du Pont, USP 2,245,535.

IG have developed a new method for the preparation of Anthrasols applicable to the anthraquinoneacridones which are not suitable for conversion into the usual sulfuric ester type because of the instability of the sulfuric esters or their inability to regenerate the parent dye on the fiber.[29, 30] The acridone is treated with phosphorus oxychloride or phosphorus pentachloride when the phosphorylated derivative (XIII) is formed, which on dissolving in aqueous sulfite or bisulfite gives the water-soluble dye (XIV). The dyes (XIV) mostly gave weak shades on development, but the derivative of Indanthrene Violet FFBN (an anthraquinonebisacridone) behaved normally like other Anthrasols. The yield of the solubilized product from the parent dye was however only 25%.



Application of the Sulfuric Esters of Leuco Vat Dyes

Processes for dyeing and printing with the Indigosols have been described in a series of patents.[31, 32] The Indigosols were originally developed for use on wool and silk, so that caustic soda required for vatting may be avoided. At present, however, the Indigosols and Soledons are more important for cotton, because cheaper and comparably fast acid-mordant dyes are available for the animal fibers. Cotton fabrics are frequently dyed with the solubilized vat colors, and the advantages are good penetration, level shades and excellent fastness to rubbing, specially in light shades. For heavy shades the vat dyes are preferred to the corresponding Indigosols and Soledons in view of cost considerations. The solubilized vat colors as a class are less substantive than the alkaline vats, and absorption can therefore be readily controlled. In actual practice, it is easier to get level dyeings with the solubilized vat dyes than with the parent dyes. For the same reason, the solubilized vat colors are specially suited for padding processes, with the consequent advantages of complete and uniform penetration and rapid production.

[29] *BIOS* **987.**

[30] *FIAT* **1313** III.

[31] Durand and Huguenin, BP 202,630; 202,632; 203,681; 218,649; 220,964.

[32] See also Bader, Chimie et Industrie Special No. 449 (1924); Peterhauser, *J. Soc. Dyers Colourists* **42,** 152 (1926); **43,** 251 (1927).

Some of the Indigosols and Soledons, however, have good substantivity, the substantivity being in general parallel to the substantivity of the alkaline vat of the parent dye. Thus the solubilized anthraquinone vat colors are usually more substantive than the indigoid derivatives.

When the solubilized vat dye has poor affinity, the dyebath may be exhausted by commencing the dyeing at about 80° and working the material in the cooling bath, whereby the solubility is decreased; Glauber salt may also be added. Uneven dyeing sometimes results, e.g., with Indigosol O, Brown IRRD and Blue IBC, as a result of exposure of parts of the fabric to atmospheric oxidation; in jigger dyeing for instance the selvedges are often dyed deeper shades for this reason. The addition of a little alkali and formaldehyde-sulfoxylate to the dyebath eliminates premature development. After impregnation, the solubilized vat color has to be developed; the reaction [$2{-}C(OSO_3Na){=} + H_2O + O \rightarrow 2{-}CO{-} + 2NaHSO_4$] involves hydrolysis and oxidation. The main method in cotton dyeing is to use sodium nitrite and sulfuric acid. Sodium nitrite (about 1%) may be added to the dyebath itself, or to the acid developing bath; the former procedure is more generally adopted, so that the developing bath consists merely of about 2% sulfuric acid. Under the right conditions the amount of absorbed nitrite is adequate for the oxidation, and the discomfort of excessive nitrous fumes being evolved, when the nitrite and acid are added simultaneously, is avoided, as well as the danger of over-oxidation due to excess of nitrite. The incorporation of small amounts of hydroquinone, *p*-aminophenol, pyrogallol, gallic acid or tannic acid to the developing bath is another method of preventing over-oxidation; such addition also counteracts the oxidation of solutions of the solubilized vat dyes when exposed to daylight.[33] Excess dye-liquor is squeezed out, and the fabric is then worked in the acid liquor for a few seconds at 50–55°. The acid is immediately washed off, preferably in an alkaline bath, and the process is completed by soaping at the boil.

Wool and silk are dyed from a neutral or faintly acid (formic and acetic acid) bath with the addition of ammonium sulfate or Glauber salt; Rongalite may be added if necessary for preventing premature oxidation. For development, dichromate is preferred to nitrite to avoid the possibility of nitrous acid reacting with the proteins. In silk dyeing, potassium persulfate may be used for oxidation in place of dichromate.

In calico printing the nitrite process is employed for direct styles. The printing paste consists of the leuco sulfuric ester, a solubilizing agent for the sparingly soluble dyes, sodium carbonate, nitrite and thickening.

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[33] Durand and Huguenin, BP 503,699.

Before development in sulfuric acid as usual, the printed goods may be steamed to get full color value. Another method, useful for resist styles, is to use sodium chlorate and acid-yielding agents such as ammonium oxalate, lactate or sulfocyanide in the printing paste; development takes place during steaming as a result of the dissociation of ammonia. In direct styles, this method is little used since many Indigosols do not develop fully; but when the cloth is padded with a solution of the solubilized vat dye, sodium chlorate, ammonium vanadate and lactate or sulfocyanide, and a white or colored resist containing for instance Rongalite as the resisting agent is printed, the resisting action is very effective on steaming. The development of the dye may then be completed by a passage through a dichromate-sulfuric acid bath. The usual vat-printing paste of vat dye, Rongalite and potassium carbonate is an effective resist for an Indigosol; thus we ultimately obtain a vat-dye resist under a vat-dyed ground, and the entire printed effect has the uniformly excellent vat dye fastness which is otherwise unobtainable. The Indigosols and Soledons are therefore valuable in calico printing.

Thiourea ("Anthrasol or Indigosol Salt NO"),[11] which prevents overoxidation by the action of excess nitrous acid, is an assistant in the application of the Indigosols (e.g., Red IFBB, Blue IBC and Olive Green IB, which are sensitive to nitrite oxidation and consequently give dull off-tone shades of diminished fastness to light and soda-boil), especially in printing by the direct and resist styles. Thiourea apparently forms a labile compound with nitrous acid, and thus regulates the oxidation. In dyeing and printing, thiourea (1–6 g. per l.) is added to the sulfuric acid developing bath. The special advantage of this addition in resist printing is when the resists are under Aniline Black and the azoics, particularly Variamine Blue combinations. A mixture of pyridine-betaine hydrochloride[19] and silver salt (Reservol BC; IG) is a useful addition to vat resists under Indigosol Blue IBC; prior to its introduction it was not possible to produce bright vat resists under this Indigosol. Phenylguanidine-*p*-sulfonic acid leads to brighter and stronger prints with leuco sulfuric esters which form sparingly soluble alkali salts.[33a]

Since a vigorous process of oxidation under acid conditions is involved in the application of the leuco sulfuric esters of vat dyes, there appears to be some evidence that, in spite of every precaution, traces of oxycellulose and/or hydrocellulose are formed, which may be detected by the usual methods (copper number, cuprammonium fluidity, Methylene Blue absorption). The oxycellulose formation is probably significant enough to enable the identification of vat dyes applied in the form of the leuco sulfuric esters.

[33a] Topham and ICI, BP 633,536.

The oxidation of the Indigosols in aqueous solution by the action of light, which gives rise to the defect of premature development in dyeing and printing processes, has been utilized in the production of color photographs.[34]

The Indigosols and Soledons can be estimated in substance by treating an aqueous solution with standard ceric sulfate solution (in slight excess) and concentrated sulfuric acid at 80–90° for a few minutes; the parent vat dye separates rapidly in readily filterable form and is then collected on a sintered glass crucible, washed, dried and weighed.[35]

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[34] IG, BP 431,072; Stewart, BP 633,634.

[35] Patni, Unpublished work.

CHAPTER XXXV

SULFUR DYES

Apart from dyes containing sulfonic groups, there are dyes belonging to various chemical and dyeing classes which contain sulfur in their composition (e.g., Methylene Blue, Primuline, thioindigoid dyes, Hydron Blue); but the group name of sulfur or sulfide dyes[1-3] is usually restricted to the dyes which dissolve in aqueous sodium sulfide forming reduction products with a marked affinity for cotton; the dyes are regenerated by air oxidation. Their essential characteristic, therefore, is the property of dyeing unmordanted cotton from a sodium sulfide bath. Sulfide dyes are thus distinguished from sulfurized vat dyes, which are best applied from an alkaline hydrosulfite solution or by similar vat dyeing processes, although dyes of both these groups (as well as some dyes of other types) are prepared by thionation or heating with sulfur, sodium sulfide or polysulfide. The technically important sulfur dyes are further characterized by the use of a limited and well-defined type of intermediate, while many organic compounds are capable of forming sulfide dyes by sulfurization under the right conditions. The great technical value of sulfur dyes is due to their low cost and high order of fastness, except to chlorine.

Troost (1861) discovered the first sulfur dye; and the first sulfur dye to be manufactured (Croissant and Bretonnière, 1873) was Cachou de Laval (CI 933), prepared by heating organic refuse (bran, sawdust, etc.) with sodium polysulfide at about 300°. Hydrogen sulfide was evolved, and sulfur combined with the substances. The higher the temperature of heating, the darker was the color of the products, which dyed brown shades improved in fastness by afterchroming. In 1893 Vidal prepared the first sulfide dye from a simple and definite intermediate; by heating *p*-phenylenediamine (and later *p*-aminophenol) with sodium sulfide and sulfur, Vidal Black[4] (StD; CI 973) was produced. There were difficul-

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[1] Lange, Die Schwefelfarbstoffe, ihre Herstellung und Verwendung, 2nd ed., Spamer, Leipzig, 1925.

[2] Morgan, Thorpe's Dictionary of Applied Chemistry, 3rd ed., Vol. VI, Longmans, London, 1929, p. 494.

[3] Jones, *Chem. Revs.* **36,** 291 (1945); Schubert, *Melliand Textilber.* **28,** 270 (1947).

[4] Vidal and StD, FP 206,405; USP 532,484.

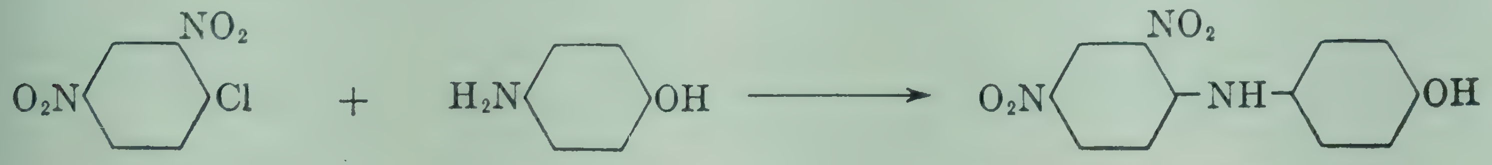
ties in repeating the reaction without variations in strength and shade, and it was then found that a relatively low temperature of 140–180° was suitable. Vidal showed that diphenylamine derivatives were formed in the course of the reaction, and to the present day diphenylamines are among the important intermediates used for the production of sulfur dyes. The first commercial success resulted from the use of the condensation product of *p*-aminophenol and 2,4-dinitrochlorobenzene, which on heating to dryness with sodium sulfide and sulfur gave Immedial Black FF extra (C) (Kalischer, 1897; CI 988).[5] This was a better dye than Vidal Black, because it was oxidized by air to a full black, did not require afterchroming and the fastness to washing and light was good. Immedial Black rapidly became a bulk manufacture. The discoveries of Vidal and Kalischer represented a great advance in the production of sulfur dyes, since they led to the realization that the future lay in the abandonment of crude and complex organic materials for thionation and the use of simple and specific intermediates. In the same year (1897) sulfur monochloride (S_2Cl_2) as a thionating agent was discovered; its use has proved to be a valuable method for the preparation of thioindigoid dyes, revived in recent patents for the synthesis of sulfur dyes of high fastness from a wide variety of intermediates. The next important discovery was that, instead of heating the solid reactants, aqueous solutions could be used, with steam heating and stirring. The reaction was hence more regular and there was less variation in the final product. At the end of the reaction the dye could be precipitated by blowing air through the mixture. It was then found that if crystalline $Na_2S, 9H_2O$ was used, it served the same purpose as the aqueous solution, giving the right proportion of water. Numerous organic compounds give sulfur dyes when heated with sodium sulfide and sulfur. Aromatic compounds of various types and even aliphatic compounds can be employed; hence there can be no common nucleus in these dyes; sulfur and sodium sulfide merely introduce certain necessary groups into compounds of the most diverse structure. Although sulfurization is a complex process, the reaction in its simplest form may be pictured as follows: $XH \rightarrow X\text{–}SH$ (soluble in alkali) $\xrightarrow{O_2}$ XS–SX (insoluble dye). The compound X–SNa has affinity for cotton, and by atmospheric oxidation the dye XS–SX is formed on the fiber. Much progress has now been made on the technical side, but attempts to isolate the sulfur dyes in pure form as individual chemical compounds and to determine their constitution have been largely unsuccessful. The complete constitution of even a single sulfur dye has not yet been established, because of intrinsic difficulties in the problem.

[5] Cassella, USP 610,541.

TECHNICAL PRODUCTION OF SULFUR DYES[6–8]

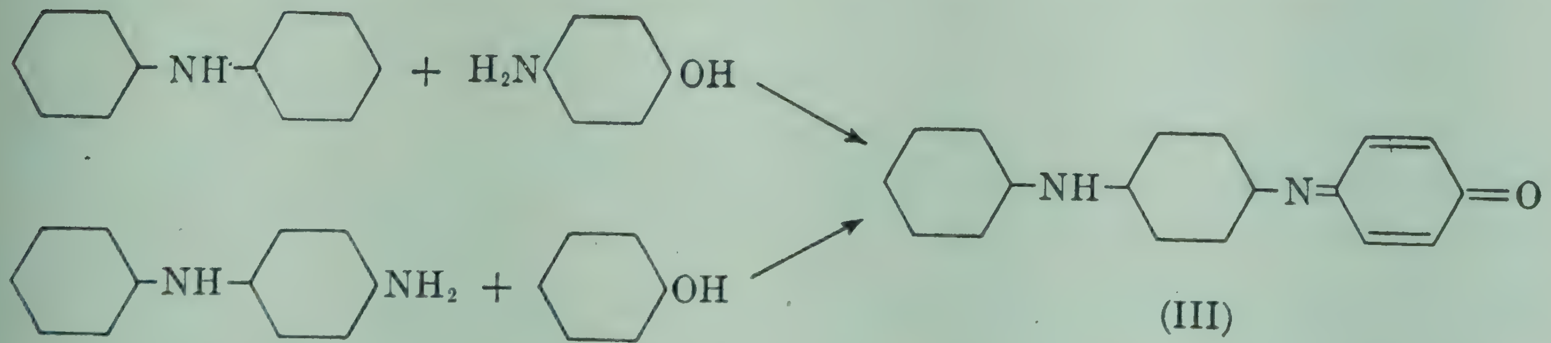
Intermediates. The main intermediates employed for thionation are aminophenols, which may be conveniently produced *in situ* from nitrophenols; diphenylamine derivatives, especially 2,4-dinitro-4′-hydroxydiphenylamine (II); nitro compounds, amines and aminosulfonic acids of the naphthalene series; indophenols; and azines. For polyamines and aminophenols liable to decomposition, it is an advantage to add the nitro compound to polysulfide solution, so that reduction is followed immediately by thionation; this is true for instance of the outstandingly important sulfur dye, Sulfur Black, which is prepared directly from 2,4-dinitrophenol.

Diphenylamine derivatives or leucoindophenols such as (II) are prepared by heating the appropriate amine or aminophenol with a chlorobenzene derivative containing nitro groups or nitro and sulfonic groups in the *o,p*-positions. With only one nitro group the reaction has to be carried out under pressure, or in the laboratory by heating the reactants with iodine as catalyst. 2,4-Dinitrochlorobenzene (I) condenses readily with amines and aminophenols in boiling aqueous alkali. A convenient method is to dissolve the aminophenol in water containing sodium bisulfite, add (I) together with about a fourth of its weight of chalk, and boil for 3–4 hours; (II) separates on cooling (yield 95%).



(I) (II)

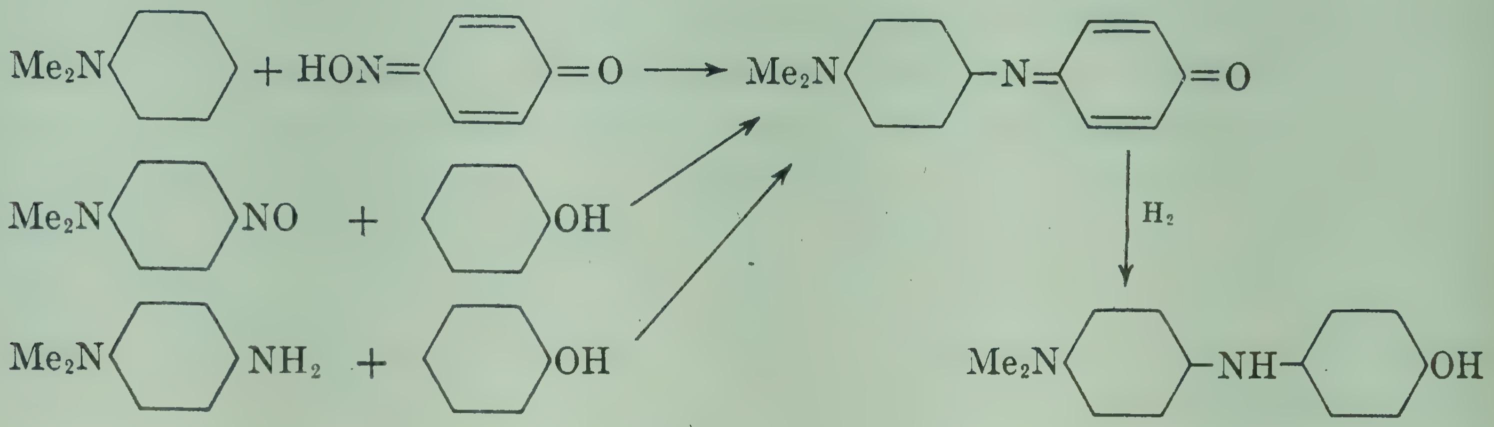
The indophenols (e.g. III) required for the preparation of sulfur dyes are prepared by two methods: (a) A mixture of a primary or secondary amine with a free *p*-position and a *p*-aminophenol, or a mixture of a phenol with a free *p*-position and a *p*-diamine, is oxidized. The usual oxidizing agent is alkaline hypochlorite at 0°. For the indophenol from



(III)

[6–8] For an account of detailed processes and plant for the production of sulfur colors, see (6) *BIOS* **983,** (7) *BIOS* **1155** and (8) *FIAT* **1313** II, III.

diphenylamine-sulfonic acid manganese dioxide can be used.[8] (b) A secondary or tertiary amine (e.g. diphenylamine; dimethylaniline; carbazole) with a free *p*-position is condensed with a *p*-nitrosophenol in presence of concentrated sulfuric acid; or a *p*-nitroso tertiary amine is similarly condensed with a phenol having a free *p*-position; of these two alternatives the former, using *p*-nitrosophenol, is the preferred method. The indophenols are easily reduced (iron and acid; neutral or alkaline hydrosulfite; sodium sulfide) to the leuco compounds (e.g. IV). This reduction is the first stage in the thionation of an indophenol, and frequently it is preferable to prepare the leuco compound first and carry out the thionation as a separate stage. Thus (IV) is manufactured by dissolving *p*-aminodimethylaniline (173 kg.) in water (10000 l.); and adding phenol (120) in water (400), ice (6000) to bring the temperature to 0°, sodium bicarbonate (124), and a mixture of sodium hypochlorite solution (1500 l. = 213 kg. chlorine) and 33°Bé caustic soda solution (225 kg.). The temperature rises to 7° and the oxidation is almost instantaneous. The precipitated indophenol is filtered, washed and digested for 2 hours at 50–60° with a solution of crystalline sodium sulfide (330) and sulfur (64) in water (940); (IV) is now in solution as the sodium salt, and is precipitated by screening the solution, cooling to 15° and adding sodium bicarbonate (280 kg.). The yield is 79% on the phenol.[7]



(IV)

The indophenols are usually blue in color, while the leuco compounds in alkaline solution are pale yellow; reoxidation can be readily effected. The indophenols are unstable and highly reactive compounds. Like other benzoquinone and naphthoquinone derivatives, they can undergo addition reactions involving nuclear substitution; thus they react with sodium bisulfite under suitable conditions to form sulfonic acids, a few of which are useful for sulfurization.

Conditions of thionation. In a thionation process the conditions have to be carefully specified and controlled, since the same intermediate can often lead to a variety of shades in accordance with the relative proportions of sodium sulfide and sulfur, solvent if any, temperature, use of pressure, and addition of metallic salts. Further alterations in shade can occur by submitting the thionated product to other treatments, especially oxidation. In general there is a deepening of color with more vigorous conditions of sulfurization, because of a continuous increase in the size of the molecule through the intervention of sulfur atoms and the formation of sulfur-containing ring systems. Under modern conditions of dyestuff manufacture, intermediates of high purity are employed, and by strict adherence to operating procedures uniform products of reproducible quality are obtained.

The main thionating agent is sodium polysulfide, prepared by heating sodium sulfide and sulfur, but sulfur alone is used for some dyes. It has been stated that the iron content of sodium sulfide is an important factor in determining the quality of some dyes; the IG specification was a maximum of 0.03% iron in sodium sulfide crystals, and if still lower iron content was necessary, sodium polysulfide was prepared from caustic soda and sulfur.[8] Nitro compounds are liable to explode with elementary sulfur, and aqueous sodium polysulfide is a safer sulfurizing agent which enables the reaction to proceed smoothly to the desired stage of thionation and the progress of the reaction to be followed readily. Fusion with sulfur is suitable for sulfur dyes of the thiazole type (Primuline analogs), which constitute many of the yellow, orange and brown dyes of the series. Sulfur dyes have been prepared by passing vapors of organic compounds over molten sulfur.[9] Sodium monosulfide can also yield sulfur dyes at high temperatures; under these conditions the sulfide undergoes conversion into sulfites, thiosulfates and polysulfides which are the effective thionating agents. Calcium polysulfide has been mentioned.[10] In thionating nitrophenols the addition of a thiosulfate accelerates the reaction and gives blacks free from uncombined sulfur, with improved shade and solubility.[11] Copper salts (mainly the sulfate) may be added to the fusion mixture; the action of copper is to give yellower reds, redder browns and violets, yellower greens, and greener blacks. The introduction of copper into the fusion mixture can also materially alter the dyeing properties. Thus Immedial Black, prepared by heating (II) with sodium sulfide, changes to blue when it is treated with an oxidizing agent (e.g. hydrogen peroxide) in substance or on the fiber; but when the same thionation is effected in presence of copper, the black is no longer susceptible to color change by oxidation.

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[9] Palmer *et al.*, *JACS* **62,** 1005 (1940); *ibid.* **52,** 3388 (1930); USP 1,884,762; *J. Org. Chem.* **15,** 177 (1950).

[10] Ellis, USP 1,187,614.

[11] du Pont, BP 364,048.

Other additions, which have been suggested with the object of modifying the shades or assisting the reaction in other ways, are the salts of zinc, chromium, manganese and iron, or the metals themselves; compounds of molybdenum,[12] tungsten, uranium, vanadium, antimony, phosphorus,[13] and mercury;[14] and potassium cuprocyanide.[15] The addition of zinc salts in the thionation of 1,8-naphthalene derivatives to form blue dyes prevents the formation of brown impurities.[16] In the fusion of an indophenol to a blue dye, manganous sulfate is a useful addition.[17] An oxidizing agent (e.g. sodium nitrite) may be added for completing the oxidation, particularly for black dyes.

Although water is adequate as the medium for many thionations, some are best carried out in alcoholic or aqueous alcoholic solution. This is particularly true of the sulfurized vat dyes, such as Hydron Blue, whose purity is considerably improved by using an alcoholic solvent; the desired shade and dyeing properties are indeed unobtainable otherwise. The low temperature (about 80°) at which thionation in ethanol solution is effected necessitates prolonged periods of reaction, but this disadvantage is more than compensated by the purity of the dye and its ready separation in easily filterable form. Butyl and amyl alcohols, glycerol, phenol, cyclohexanol,[18] cellosolve,[19] petroleum oils[20] and the product obtained by heating ethylenediamine with sulfur (which functions also as thionating agent)[21] are among the solvents which have been suggested. Butanol was generally employed by the IG. The addition of sodium nitrite to some solvent thionations effects a considerable reduction in time.[8]

Manufacturing methods[6, 7, 8] fall into two distinct classes: (1) dry heating or baking; and (2) heating the reactants in solution. The temperature of thionation is a vital factor since the yield and shade of the ultimate product are materially affected by changing the temperature; the same thionation mixture may give a blue, green or brown dye at relatively low temperatures and a black at high temperatures. Cast-iron vessels are suitable for both the procedures; but in view of the corrosive character of thionation mixtures, iron alloys (e.g., with a content of up to 33% chromium and 2–2.5% carbon) and other special materials of construction have been considered.[22] In the baking or dry fusion process, carried out at high temperatures (200–300°), the heating may be carried out by direct fire or by means of an oil jacket to avoid local overheating. Effective agitation of the mixture is necessary, and heavy duty agitators or rotary bakers containing balls or rods may be used. For the second process of condensation in solution the standard type of plant is a 300–2000 gallon reaction kettle (which may be lead-lined), jacketed for superheated steam (about 100 lbs. pressure), and provided with a mechanical agitator, reflux condenser, manhole for the addition of the reactants, thermometer tube, and an inlet tube for applying suction or compressed air. For aqueous or alcoholic sodium polysulfide fusions, sodium sulfide and sulfur are first digested until a solution of the polysulfide is obtained, and the intermediate to be thionated is then added. Thionation in aqueous or alcoholic solution under reflux, so that dye formation takes place at about 100°, is especially valuable for sulfur blacks, blues from indophenols, and violets from the azines. Temperatures of 100–130° are generally sufficient, but if higher temperatures are necessary the reaction is carried out under pressure in an autoclave. Heating the aqueous or alcoholic solution under pressure sometimes leads to products with improved tinctorial value. Immedial Black, prepared in this manner from 2,4-dinitro-4′-hydroxydiphenylamine, separates as a crystalline, dark blue lustrous powder dyeing very intense black shades.[2]

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[12] IG, BP 359,254; 359,273; 359,276.

[13] IG, FP 707,027; 705,930.

[14] Bolotina, RP 50,611.

[15] Wutke and Hagge, USP 1,609,927.

[16] Bayer, DRP 116,655.

[17] StD, DRP 222,406; FP 406,225.

[18] IG, BP 319,860.

[19] Johnson, Strouse, and du Pont, USP 2,125,924; Lubs, Strouse and du Pont, USP 1,944,250; du Pont, BP 388,814; ICI, FP 772,160.

[20] Nikolaev, RP 40,474; National Aniline, BP 181,673.

[21] Norman and Industrial Dyestuff Corporation, USP 2,136,016–7.

The production of sulfur dyes is always carried out by batch processes, but continuous processes have been suggested.[23]

The progress of the reaction is followed by dissolving a sample in water or aqueous sodium sulfide and carrying out a dyetrial; or by precipitating the dye and excess sulfur with acid and then estimating the unthionated amine in the acid filtrate. Depending on the nature of the intermediates, the usual method of diazotization and titration with alkaline β-naphthol or colorimetric methods based on conversion into azo dyes or indophenols may be employed. The method of isolation of the dye varies according to the process of thionation and the character of the dyestuff. Products of the baking process may be merely ground up and standardized, or they may be boiled with caustic soda or sodium sulfide solution and treated like the wet fusion products. The dye may then be precipitated from the alkaline solution by acidification, or by air oxidation and salting out if necessary. Alkaline air oxidation, e.g. in the thionation of hydroxydiarylamines, results in brighter shades.[24] Filtration is generally carried out in a filter press, but for products made on a large scale rotary filters may be employed. A solution of the dye in aqueous sodium sulfide may be dried down on double drum dryers operated at atmospheric pressure or in vacuum. The dyes are then ground and standardized, using sodium sulfate or carbonate (or occasionally phosphate) as diluent. The tendency of some sulfur dyes to ignite during grinding is minimized by drying to very low moisture content.[8] Sulfur dyes may be marketed in water-soluble form by mixing them with excess sodium sulfide or hydrosulfide and hygroscopic agents (e.g. sodium formate).[25] Stable dispersions of sulfur dyes can be made in primary and secondary alkanolamines.[25a]

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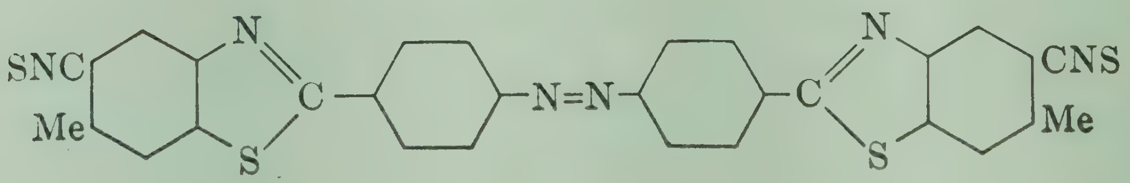
[22] Pershke and Graevskaya, *Org. Chem. Ind.* (*U.S.S.R.*), **5**, 126 (1938).

[23] Amiantov and Bobrovskiĭ, RP 54,111.

[24] Strouse and du Pont, USP 2,156,071; Hess and National Aniline, USP 2,152,693.

The hydrogen sulfide evolved during thionation is absorbed in alkali to prevent health hazards and to recover the sulfur as sodium sulfide or hydrosulfide. The recovery of sodium thiosulfate from aqueous thionation mixtures is another important aspect of sulfur dye manufacture. Thiosulfate of relatively high purity can be readily isolated by evaporating the filtrate from which the sulfur dye has been separated; in the large scale manufacture of a dye such as Sulfur Black, the recovery of sodium thiosulfate is a considerable factor in the economy of the process.

Sulfur dyes other than products of sulfur fusion. Compounds containing thiocyano (—CNS) or xanthato (—CS_2—OEt) groups function as sulfur dyes, and by using appropriate aromatic or heterocyclic ring systems, dyes with good fastness to washing, bleaching and light can be obtained.[26] Thus the diamines, prepared by reduction of the product obtained either by nitration of 4,4′-bis-(6-methylbenzothiazyl-2)-azobenzene or by oxidation of nitro-2-(*p*′-aminophenyl)-6-methylbenzothiazole with hypochlorite in cellosolve solution, are tetrazotized, and the diazonium groups replaced by —CNS or —CS_2—OEt. The products dissolve in aqueous sodium sulfide and act as sulfur dyes, or may be hydrolyzed to the dithiols, which are oxidized, for instance by nitrobenzene-*m*-sulfonic acid, to polysulfides, which are similarly used, giving



orange-yellow shades of good fastness to washing, bleaching, and light. Alternatively, the intermediate may be converted into the disulfonic acid by sulfonation, or the same compound may be produced by oxidizing dehydrothiotoluidinemonosulfonic acid; the disulfonic acid is converted into the acid chloride with phosphorus pentachloride, and condensed with thiocyanoarylamines or their *N*-substituted derivatives. The products act as sulfur dyes, the thiocyano groups being converted into thiol in the sodium sulfide bath. They may be first hydrolyzed by alkali and oxidized to polysulfides.

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[25] IG, BP 419,817; 429,350.

[25a] Conn and American Cyanamid, USP 2,472,052.

[26] Haddock and ICI, USP 2,439,804.

An important advance in the production of sulfur dyes has been described in recent ICI-du Pont Patents.[27] Organic dyes or pigments of the anthraquinone, indigo, thioindigo, phthalocyanine, thiazole, indophenol, acridine, azine, dioxazine, perylenetetracarboxylimide, dibenzopyrenequinone, azo, or sulfur classes are heated with the aluminum chloride-sulfur monochloride complex ($AlCl_3, 2S_2Cl_2$) made by heating aluminum chloride (20 parts) and sulfur monochloride (42) at 90–95° for 36 hours. For example, copper phthalocyanine (50) is added at room temperature to the complex (200), the temperature is raised to the boil, more of the complex (200) is added, and after boiling for 40 minutes, the melt is poured on ice, collected, and washed with hot dilute aqueous sodium hydroxide; cotton is dyed bright green from a bath of aqueous sodium sulfide. Other metallic salts, e.g. zinc chloride, iron chloride, or copper chloride, may be added to the melt. Indigo (105) and the complex (161) in carbon tetrachloride (1500), stirred at 80° for 2 hours, give a green dye for cotton. Among other dyes similarly treated are 6,6′-dichloro-4,4′-dimethylthioindigo (bluish-red), carbazole-indophenol (olive-green), 3,8-diamino-4,7-dimethylacridine (reddish yellow), the azo dye (1-naphthylamine-2-sulfonic acid → 2-hydroxy-3-naphthoic acid) (red on wool), indanthrone (light blue), and perylene-3,4,9,10-tetracarboxy-*N*,*N*′-diphenylimide (red).

In the phthalocyanine series (see Chapter XXXVII), blue and green dyes applicable from a sodium sulfide bath have been made by treating a phthalocyanine containing one or more sulfonyl chloride groups with a phosphorus sulfide. Copper phthalocyanine tetrasulfonyl chloride heated with phosphorus pentasulfide in nitrobenzene solution gives a green sulfide dye.[28]

SHADES OF SULFUR DYES

Since little is known regarding the precise constitution of the sulfur dyes, while many hundreds have been made, it is customary to classify the commercial dyes of this class in accordance with their color. The relative commercial importance of sulfur dyes of various shades is indicated by the 1941 production figures (in 1000 pounds) in the United States: Black 17,414; blue 3,644; brown 2,885; green 875; maroon 812; yellow 570; olive 397; tan 335; orange 127.[29]

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[27] BP 573,831; du Pont, USP 2,369,666–8; 2,504,153; IP 30698.

[28] Wood and ICI, BP 588,696.

Among the group names for the sulfur dyes of commerce are Immedial (C; IG), Kryogene (BASF), Thiogene (MLB), Pyrogene (Cb), Eclipse (Gy), Thionol (ICI), Thional (S), Katigen (GDC), Calcogene (Calco), and Sulfogene (DuP).

Yellows, oranges, browns and olives. These dyes usually lack light fastness, and therefore constitute minor products in the sulfur dye range. They are made chiefly from *m*-toluylenediamine (V), to which benzidine (VI) may be added. By heating (V) with sulfur at 190°, and then heating the orange product, m.p. 145°, with aqueous sodium sulfide or sodium hydroxide at 110–120° until the product is solubilized, and finally precipitating with acid, Immedial Yellow D (Weinberg and Lange, 1902; CI 948), the first yellow sulfur color of commercial value, was produced. By carrying out the thionation at a higher temperature (250°), the product was Immedial Orange C (C; CI 949). By altering the proportion of sulfur and thionating at a still higher temperature, yellowish brown dyes can be obtained. Various yellows are obtained by heating *N*-acyl diamines with sulfur. An example is Eclipse Yellow G (Gy; CI 951), prepared by heating the mono- or diformyl derivatives of *m*-toluylenediamine with sodium sulfide and sulfur in aqueous solution, and then at 240°; the intermediates are made by the action of boiling formic acid on the amine.[30] A compound of the composition $(C_{17}H_{14}N_4S_{6.27})_n$ has been isolated from the thionation product of monoformyl-*m*-toluylenediamine.[31] The product from the diformyl compound is regarded as a complex polysulfide $(C_{17}H_{12}N_4S_2)_6$ $(S{-}SH)_5$ $(S{-}S{-}SH)_5$, which oxidizes with alkaline permanganate to a polysulfonic acid $(C_{17}H_{12}N_4S_2)_6(SO_3H)_{10}$.[31] Thiazole residues are apparently formed in these reactions (cf. dehydrothiotoluidine and Primuline), since a nuclear alkyl or an *N*-alkyl group is essential and *m*-phenylenediamine itself does not yield such yellow and brown dyes.[32] Such thionations may be carried out in two stages by preparing an authentic thiazole derivative first and then heating it (alone or mixed with an aromatic amine) with sodium sulfide or sulfur.

In the Pyrogene Yellows (Cb; CI 954) which were discovered more or less simultaneously with Immedial Yellow D, the intermediates were the Schiff's bases prepared by condensing *m*- or *p*-nitrobenzaldehyde with

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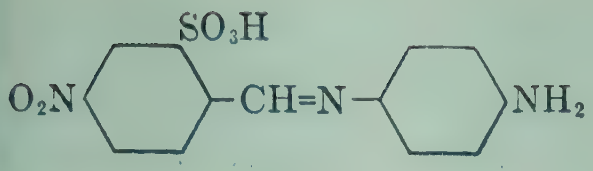
[29] U. S. Tariff Commission.

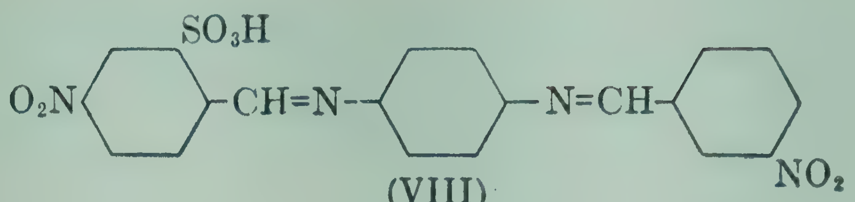
[30] Geigy, DRP 138,839; 145,762–3.

[31] Mazumdar and Watson, *JCS* **117**, 830 (1920).

[32] Jaekel, USP 1,140,745.



(VII)



(VIII)

aromatic amines and aminophenols. The corresponding dihydro compounds or benzylamines prepared by condensing nitrobenzyl chlorides with amines could also be employed. Thus, (VII) gave greenish yellow and (VIII) yellow dyes.[33] *p*-Hydroxymethyleneaniline and *p*′-nitrobenzylidene *p*-aminophenol led respectively to brown and olive dyes. Alkyl (C_{1-4}) carbanilates (phenylurethans), e.g. Ph-NH-COOMe in which the nucleus may contain Me, NH_2 or other substituents, give yellow to orange dyes.[34] Aryldiguanides, mixed with benzidine or *m*-toluylenediamine, give yellow to orange dyes.[35] *N*-Alkyl derivatives of benzidine, the naphthylamines and their sulfonic acids (e.g. 1-ethylaminonaphthalene-8-sulfonic acid) yield yellow to brown dyes.[36] Kryogene Yellow R (BASF; CI 953) was obtained by heating 5-amino-2-methylbenzimidazole with sulfur at 200–230°, and then with sodium sulfide at the same temperature; the intermediate was prepared by the reduction of 2,4-dinitroacetanilide with iron and acetic acid. A free amino group is present in the dye, and may be diazotized on the fiber. When 5-nitro-2-methylbenzimidazole was thionated in admixture with benzidine, a greener yellow was obtained. Fastness to chlorine has been claimed for the yellow sulfur dyes prepared from *N*-alkyl, aryl or aralkylcarbazoles, preferably admixed with benzidine or tolidine.[37]

The Immedial Yellows, Oranges, Yellow Browns and Olives in the current IG range are made by fusion with sulfur in a rotary baker. The quantity of sulfur and time of fusion are stated in Table I.[7] Except for Yellow G and RR and Olive GN which are merely broken up and milled, the melts are finally boiled with 15–35% caustic soda solution for several hours; the dyestuff is precipitated by acid, filtered and dried. With some of the Immedials (e.g. Olive FF, Yellow Olive G, Green Yellow G), the melt is dissolved in boiling sodium sulfide solution. For Orange C and RRT, the aqueous caustic soda solution is filtered, salt is added, and the solution is dried on a drum dryer. For Yellow Brown G, the melt is dissolved in aqueous sodium sulfide, caustic soda and salt; the solution is heated to 240° and finally at 240–250° in a rotary baker.

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[33] Ciba, DRP 135,335.

[34] Bigelow and du Pont, USP 2,234,018.

[35] Bigelow, Cole, and du Pont, USP 2,263,562.

[36] DRP 205,104.

[37] Cassella, DRP 475,014.

TABLE I

Intermediates	*Sulfur (kg.)*	*Temperature, °C.*	*Time in hours*
Immedial Yellow D[6]—(V) + (VI)			
Immedial Yellow FR[6]—(V) + *p*-Phenylenediamine			
Immedial Yellow FRR[6]—Nitro-acet-*p*-toluidide + (VI)			
Immedial Yellow G extra—Dinitroacetanilide (133) + phthalic anhydride (93)	94 (+280 kg. $Na_2S, 9H_2O$)	130	11
Immedial Yellow GG—Dehydrothiotoluidine (98) + (VI) (77)	500	190–225	27
Immedial Yellow 3GT—*o*-Tolidine (129) + *p*-nitroaniline (55)	220	180–250	8
Immedial Yellow R extra—Acet-*o*-toluidide (39) + (VI) (126)	429	130–245	16
Immedial Yellow RR—Diformyl-(V) (100) + (VI) (67)	400	170–220	15
Immedial Yellow RT extra—Monothiourea of (V) (72)[38] + (VI) (72)	600	200–210	16
Immedial Yellow 4RT extra—(V) (85.5), (VI) (42) + *m*-nitroaniline (36)	600	220–240	15
Immedial Yellow 6RT extra—(V) (117) + *m*-phenylenediamine (58)	420	230–250	16
Immedial Orange C—(V) (135)	480	215–220	>10
Immedial Orange RRT extra—(V) (135)	480	250	15
Immedial Orange FR Base—(V) (80) + Diphthaloyl-*p*-phenylenediamine (34)	334	210–215	10
Immedial Orange FRR Base—2-Nitro-acet-*p*-toluidide (12.3) + (VI) (58)	142	180–230	12
Immedial Yellow Brown G—(V) (213)	450	210–250	9
Immedial Yellow Brown G26—(V) (160) + 2,6-toluylenediamine (40)	428	245	12
Immedial Yellow Brown O—(V) (36.6) + *o*-aminophenol (7)	135	220–230	4
Immedial Yellow Olive G; Green Yellow G—(V) (93.5 or 75) + *p*-nitroaniline (47 or 63) + *p*-phenylenediamine (40 or 16)	380 (or 287) (soda ash 1.5)	165–240	12

Baking a mixture of *m*-toluylenediamine (80) and *p*-nitroaniline (48) with sulfur (283) at 200–210° the product is Immedial Yellow-Olive 3GR; with increasing proportions of *p*-nitroaniline, Olive 2G and Green-Yellow G are obtained. Olive 3B results from the sulfur fusion of *m*-dinitrobenzene; FF extra uses *o*-toluidine and *p*-phenylenediamine. For Olive GN an aqueous solution of *p*-nitrophenol (150), sodium sulfide (550), sulfur (115) and sodium hydrosulfide (18.5 as H_2S) is boiled, concentrated, heated to 290° in 17 hours, and finally baked at 290–300° for 7 hours. Olive B is prepared by drying down a mixture of Immedial Dark Green B and Yellow-Brown G.[6, 7]

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[38] Ref. 6 mentions the thiourea from *p*-xylidine for Yellow RT.

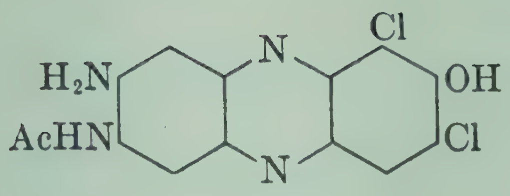
Diphthaloyl-*p*-phenylenediamine, required for Orange FR, is prepared by heating *p*-phenylenediamine with phthalic anhydride and water in presence of a little sodium bisulfite at 118° under pressure for 18 hours. Baking a mixture of *m*-toluylenediamine and *m*-nitroaniline with sulfur gives Immedial Orange-Brown RL; replacing *m*-nitroaniline by 4-nitro-*o*-toluidine, the product is the 3RL brand.[6]

When the thionation of *m*-toluylenediamine is carried out in presence of oxalic acid, or when the pre-formed oxalyl derivative is thionated, dyes (Eclipse Brown, Gy; CI 937) yielding fast catechu-brown shades are obtained. Thiocatechine (StD; CI 936) was a brown dye produced by heating *p*-aminoacetanilide with sodium sulfide and sulfur. The influence of the acetyl group is interesting since *p*-phenylenediamine under the same conditions gives a greenish-black. When Thiocatechine was digested with sodium bisulfite, the product was the soluble Thiocatechine S.

Thion Brown (K; CI 944) was made from the azo dye obtained by coupling diazotized aniline with *m*-toluylenediamine. Nitroaminodiphenylamines yield brown sulfur dyes (e.g. Sulphine Brown, Cotton Brown; CI 938). Immedial Dark Brown A (C; CI 939) was made from (II). The thionation of 1,8-dinitronaphthalene, after prior reduction with sodium bisulfite, gave Kryogene Brown A (BASF; CI 940).

Immedial Browns (IG) are made mainly by dry fusion with sodium polysulfide, with the addition of copper sulfate in some cases. Immedial Cutch BF is prepared by heating the azine (IX) with aqueous sodium sulfide, sulfur and copper sulfate at 105–107° for 30 hours; the azine (IX) is obtained by the usual manganese dioxide-sulfuric acid oxidation of a mixture of 2,4-diaminoacetanilide and 2,6-dichloro-4-aminophenol. For Brown BR a mixture of 1,5-dinitronaphthalene (138), sodium sulfide (585), sulfur (238), cresol (75), copper sulfate (34), caustic soda (164) and salt (200) is baked at 265° for 14 hours. β-Naphthol, caustic soda, sodium sulfide and sulfur at 270–280° give Brown T. Immedial Dark Brown S is obtained by baking 1,8-dinitronaphthalene with sulfur and sodium sulfide. The GL brand is made similarly from 1-amino-5-naphthol; precipitation of the color with acid gives Immedial Fast Dark Brown B. Immedial Dark Brown R is prepared by dry fusion of (II) with sulfur and sodium sulfide; addition of copper sulfate, caustic soda and dextrose gives Dark Brown A. Immedial Black Brown A, which has good fastness but poor solubility, is made by sulfurizing brown coal in a rotary baker with sulfur and sodium sulfide; the G and GN brands are made from crude cresol.[7]

New yellow, olive and brown sulfur dyes with light fastness 6–7 have been made by IG by the thionation of decacyclene or its nitro derivatives.[8, 38a] The hydrocarbon is a product of the action of sulfur or lead oxide on acenaphthene at high temperature.[38b] Immedial Cutch 4RL was produced by baking decacyclene with five times its weight of sulfur at 350°. Immedial Cutch RL and Yellow Brown GL were prepared respectively from hexanitro and trinitro derivatives of decacyclene. For khaki shades coronene and nitrocoronenes have been suggested.[39]



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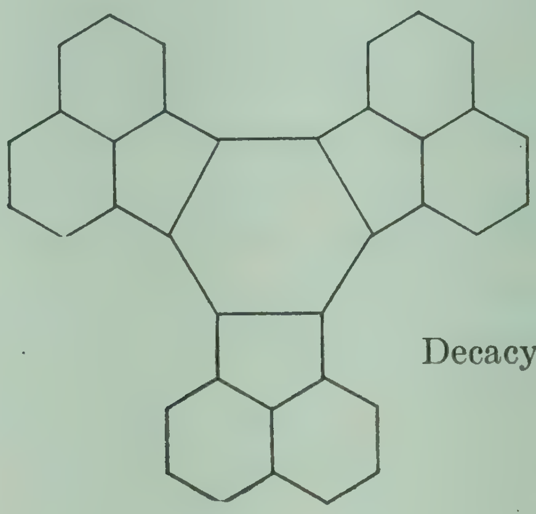

Decacyclene

Thionation of *m*-toluylenediamine, its acyl derivatives, *C*-alkylphenols and 2-methylbenzimidazoles has been studied recently by Konishi.[40] Brown sulfur dyes "fast to washing, chlorine and light" are prepared by the sulfurization of 9-phenyl-1,2,4-trichloro-3(10)-phenothiazone, which is obtained by the condensation of 2-amino-3-mercaptodiphenyl with chloranil.[41] *N*-Phenyl derivatives of aminonaphtholsulfonic acids (e.g. J- and γ-acid) give brown dyes of "excellent fastness to light and chlorine."[42] Thionation of a mixture of furfuraldehyde and 1-amino-8-naphtholdisulfonic acid gives brown dyes.[43] Brown to olive and gray dyes are produced by sulfurizing ceramidonines;[44] and dark brown

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[38a] IG, DRP 653,675; 655,487; General Aniline Works, USP 2,151,513.

[38b] Dziewoński, *Ber.* **36**, 962 (1903); *ibid.* **51**, 457 (1918).

[39] General Aniline and Film, USP 2,222,482.

[40] *J. Soc. Chem. Ind. Japan*, **48**, 45 (1945) *et seq.; Chem. Abstracts* **42**, 6539 (1948).

[41] Steiger and American Aniline, USP 2,412,922.

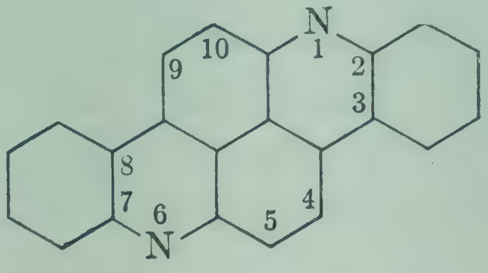
[42] Chapman and ICI, BP 418,444.

[43] Perkins and National Aniline, USP 2,182,350–1.

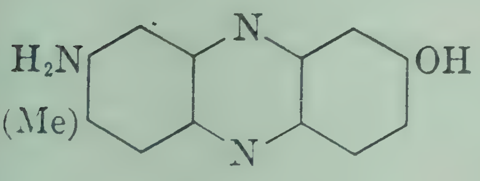
[44] Zerweck, Hechtenberg, and General Aniline and Film, USP 2,321,787.

dyes from 4,5,9,10-dibenzo-3,8-diazapyrene.[45] 2,3,7,8-Dibenzo-1,6-diazapyrene (X) is obtained in 65% yield by the oxidation of 1,5-dianilinonaphthalene with gaseous oxygen in presence of aluminum chloride at 320–330°.[46] Sulfur fusion of (X) at 220° gives a yellowish brown dye with good light and wash fastness and better chlorine fastness than the Immedial Browns; but the shades deteriorate on storage.[8]

(X)



Red to violet dyes. Nothing approaching a clear red has been made among the sulfur colors, and it is doubtful if such a reaction can produce a bright red. Pure scarlet and violet dyes are also unavailable, but brownish shades of red and violet can be prepared by the thionation of red dyes of the azine class. The redness and fastness are stated to be improved by the addition of copper and other metallic salts. The first commercial dye of this type was Immedial Maroon B (C) (Weinberg, 1900; CI 1012), prepared by fusion of the azine (XI) with sodium sulfide and sulfur at about 150°. Thionation of (XI) with aqueous sodium polysulfide in presence of copper sulfate at 115° gives Immedial Prune S.[7] The aqueous thionation of the azine from *m*-toluylenediamine and *p*-aminophenol gives Immedial Red Brown 3B; adding copper, the product is Immedial Bordeaux G. Immedial Red Brown 6R is prepared by the aqueous sulfurization of the azine from 2,6-dichloro-4-aminophenol and *m*-toluylenediamine; the effect of the two chlorine atoms is to give redness and brightness. Immedial Red Brown CL3R is prepared from the thiazone (XII), obtained by the condensation of 3-mercapto-*p*-toluidine with chloranil.[7] Immedial Red Brown CL4B is a similar dye, prepared from the *p*-phenetidine analog of (XII).[8] The azine (XIII) (250 kg. of 40% paste) from 4-ethylamino-*o*-toluidine and *p*-nitrosophenol



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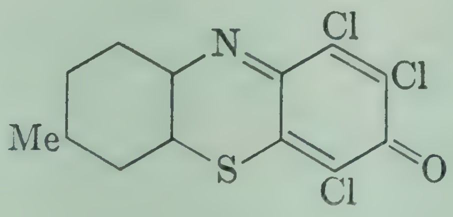

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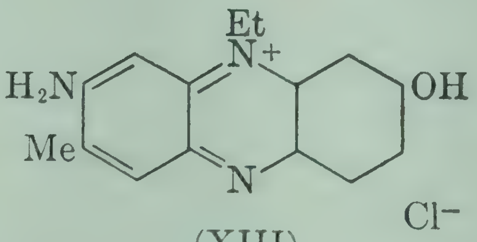

(XIII)

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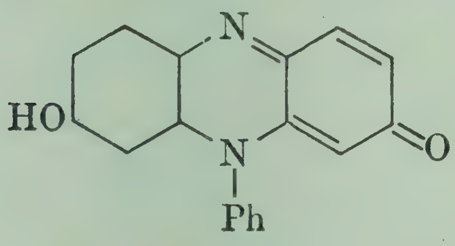
[45] Zerweck, Schutz, Hechtenberg, and General Aniline and Film, USP 2,281,968; IG, FP 872,005.

[46] Clemo and Dawson, *JCS* 1114 (**1939**).

by fusion for 15 hours at 190° with sodium sulfide crystals (1816), sulfur (408) and copper sulfate (32) gives Immedial Purple C; the mixture is evaporated down until the required boiling point is reached.[6] One of the reddest sulfur dyes, Thiogene Purple (MLB) (Schmidt, 1905; CI 1010), was made by heating the azine dye (XIII) with aqueous sodium sulfide at 115–135° under reflux or in an autoclave. Thionol Purple 2B (Lev.; CI 1009) was produced by the thionation of the azine obtained by oxidizing the indophenol from *p*-nitrosophenol and the condensation product of *m*-toluylenediamine and formaldehyde bisulfite. Copper, cobalt, or nickel salts may be added.[47] These bordeaux-red dyes become bluer by raising the fusion temperature.

Safranole (XIV), which may be prepared by the condensation of *p*-nitrosophenol with *m*-hydroxydiphenylamine or the alkaline hydrolysis of phenosafranine, yields blue-violet dyes. Thiogene Violet B (MLB; CI 1008) is of this type. Thion Violets (K) (CI 1007, 1010) were prepared by thionating various phenosafranines and rosindulines containing hydroxyl groups. Thionation of azines such as (XV) or indophenols such as (XVI) gives violet dyes of high intensity and good washing fastness.[48]



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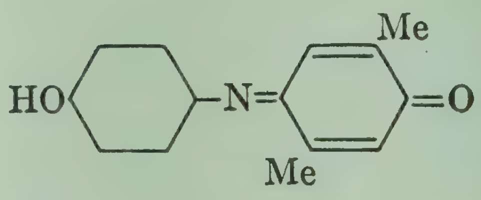

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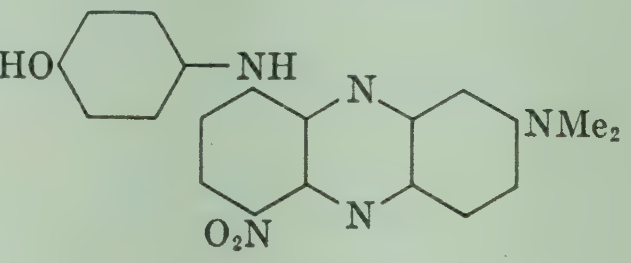

(XV)

Immedial Corinth B (Thiogene Dark Red G, R; CI 1011) is the product of the aqueous thionation of 2,4-dinitro-2′-hydroxydiphenylamine or the 5-chloro derivative; the dye has poor fastness and is only made for shading purposes.[6, 7] Immedial Violet 2B is prepared by thionating the indophenol from 2,4-diaminoacetanilide and *p*-nitrosophenol; the indophenol (480 kg. of 25% aqueous paste), sodium sulfide crystals (530), sulfur (205) and water (100 l.) are heated under reflux for 30 hours at 110° (boiling point adjusted by evaporation of the reaction mixture); the dye is salted out and filtered; the press cake is stirred up with dilute caustic soda solution and oxidized by blowing air.[6] Thionation of 4-amino-3-methyl-4′-hydroxydiphenylamine (200) with sodium sulfide (266 of 60%) and sulfur (429) in boiling butanol (1250 l.) during 60 hours gives Immedial Indone Violet B. Thionation of the oxazone (XVII) gives Immedial Bordeaux 3BL, which is a bright dye of high tinctorial power.[8]

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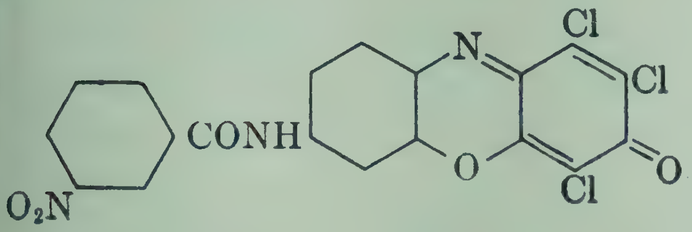
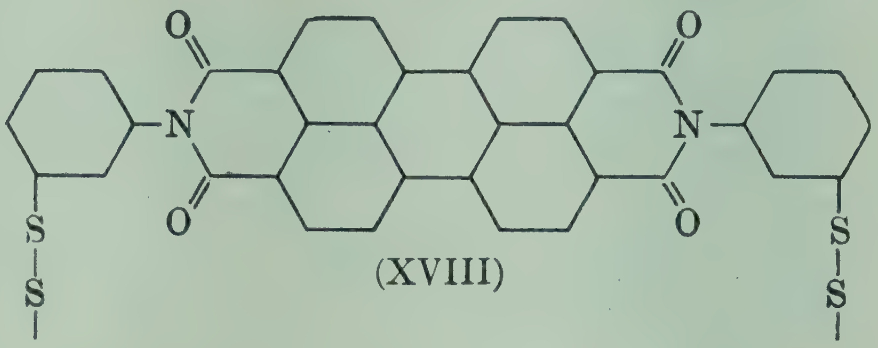
[47] Vlies, *J. Soc. Dyers Colourists* **29,** 316 (1913).

[48] Kalle, DRP 144,157; 152,373; 160,790; 160,816; 165,007; Cassella, DRP 191,863.

A new type of red sulfur dye (XVIII) is derived from 3,4,9,10-perylenetetracarboxylic *bis-p-* or *m*-aminophenylimide. By tetrazotizing such a diamine, and then treating with alkali thiocyanate, the *bis*-thiocyano derivative is formed; on hydrolysis to the mercaptan and oxidation, a red sulfur dye is obtained, which is applicable in the usual way from a sodium sulfide bath and is claimed to be brighter and faster than the sulfur dyes previously known.[49]



(XVII)



(XVIII)

Blue and green dyes. Blue sulfur dyes are technically important, being next to the black dyes in production figures.

Kalischer (1897) observed that the oxidation of Immedial Black FF in substance or on the fiber with hydrogen peroxide converted it into a blue (Immedial Blue C; CI 988). The oxidation in substance may be conveniently carried out by suspending the thionation product in aqueous alkali and blowing air at 40–45°, until the desired shade is obtained; Immedial Direct Blue B extra and RL extra (IG) are prepared in this manner.[6] Thus for Immedial Direct Blue B, the indophenol (II; 1500 kg.), sodium sulfide crystals (3300), sulfur (1760 in the form of sodium tetrasulfide solution, 3900 l.) and sulfur (540) are heated at 106° for 3 hours, and after adding salt (250) at 109–110° for 10 hours. The melt is diluted to 9000 l., and the dyestuff is filtered. The press cake is made up with water to 12000 l. and mixed with 28.8% caustic soda solution (1050 l.). Air is blown in for about 16 hours; the reaction is exothermic and the temperature is maintained at 40–45° by coil cooling. The dyestuff is salted out and filtered. The press cake is mixed with soda ash, and the homogeneous paste (40–45% solids) is dried on a rotary dryer. Blue RL is prepared by a similar process with differences in the conditions of sulfurization and oxidation.[6] When (II) is thionated under the conditions used for Blue RL, the product treated with a solution of "dithioglycolic acid" prepared from chloroacetic acid and sodium polysulfide at 95° for a few hours, and this condensation product then oxidized, Immedial Direct Blue 3RL, which dyes a much redder blue than Blue RL, is obtained.[8]

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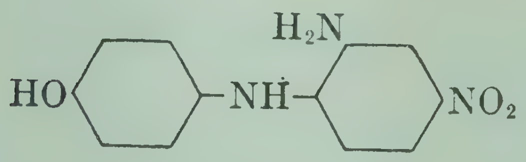
[49] Haddock and ICI, BP 547,853.

An early discovery of a reddish blue sulfur color was Pyrogene Direct Blue (Cb) (Bertschmann, 1900; CI 956), prepared from the diphenylamine derivative (XIX) or the parent dinitro compound (II) by heating with sodium tetrasulfide and alcohol at about 145° in an autoclave. The bluish violet shades, intensified by aftertreatment with hydrogen peroxide, were claimed to be fast to chlorine, light and scouring agents.[50] When the thionation temperature was raised to 170°, Pyrogene Grey, which was no longer affected by oxidizing agents, was produced. When (XIX) was heated with carbon disulfide and the thiocarbamide thionated, a bluish-gray dye, Thion Blue B (K; CI 962), changed to pure blue on the fiber by treatment with hydrogen peroxide, was obtained; aftertreatment with stannic chloride increased the fastness.[51] The first pure blue sulfur dye, however, was Immedial Pure Blue (C) (Weinberg and Herz, 1900; CI 957), obtained from the leucoindophenol (IV) heated with sodium sulfide and sulfur in aqueous solution at 110–115°. Immedial Brilliant Blue CLB (IG) is now made by the thionation of (IV) (660 kg.) with crystalline sodium sulfide (960) and sulfur (572 in the form of tetrasulfide liquor and sulfur) in boiling alcohol (660) for about a week. The alcohol is distilled off, the residue diluted with water and the dye precipitated by air-blowing and subsequent addition of hydrochloric acid (60). The still alkaline suspension is diluted, filtered, and the dyestuff dried at 60°.[7] Eclipse Blue (Gy)(Ris, 1901; CI 958) was prepared from (IV) by converting it into a sulfonic acid by means of sodium sulfite, thionating the sodium salt with sulfur and crystalline sodium sulfide at about 140°, and precipitating the dye by air, hydrogen peroxide or alkaline hypochlorite. The pure blue shades on cotton were claimed to be very fast.[52] The bisulfite compound, $C_{14}H_{12}ON_2S_2$, $NaHSO_3$, $2H_2O$, was the first crystalline derivative obtained from a sulfur dye,[53] but Gnehm and



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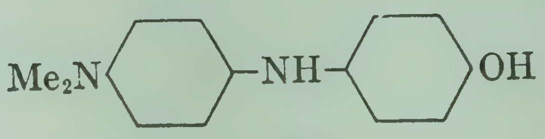

(IV)

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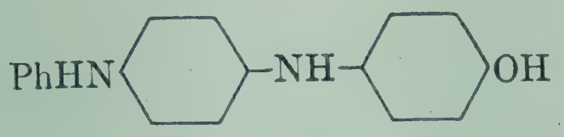
[50] Cassella, DRP 137,784.
[51] Kalle, DRP 139,099.
[52] Geigy, DRP 129,325.
[53] Cassella, DRP 134,947.

Bots[54] have recorded analytical figures which are not in agreement with this formula.

The indophenol from *p*-aminophenol and *o*-toluidine, which is the intermediate for Immedial Indone Violet B, gives with aqueous sodium polysulfide blue dyes, Immedial Indone B, R, 2R (CI 959); the variations in the tone are produced by slight changes in the thionating conditions.[6] These dyes have "a remarkable affinity for the cotton fiber."[55] The analogous dye from (XX) is Pyrogene Indigo (Cb; CI 961); the thionation is effected in alcoholic solution with sodium pentasulfide at about 120° under pressure. Immedial Indone BBF and IBN are IG dyes made from the same intermediate (XX). Other examples of Immedial Blues made from leucoindophenols are: New Blue BL (*p*-Nitrosophenol + diphenylamine-4-sulfonic acid); New Blue FBL (*p*-Aminophenol + diphenylamine-4-sulfonic acid); New Blue G and Indogen BT (Phenol + *p*-aminophenol; this is a true indophenol, as distinct from the others which are indoanilines); New Blue 3GL (*p*-Nitrosophenol + diphenylamine-*o*-carboxylic acid). Immedial New Blue 4GL, the thionation product of (XXI), and Immedial New Blue 6GL, the thionation product of the indophenol from 4-acetamidodiphenylamine, are new dyes which do not bronze in heavy shades, but have slightly lower washing fastness than some of the older Immedial Blues. Dyes made similarly from 4-acetamidodiphenylamine-2-carboxylic acid and 2-sulfonic acid have been found to have very good fastness to light. In the preparation of indophenols from sulfonated diphenylamines by oxidizing mixtures with *p*-aminophenol, the quality of the manganese dioxide used for oxidation is very critical.[8]



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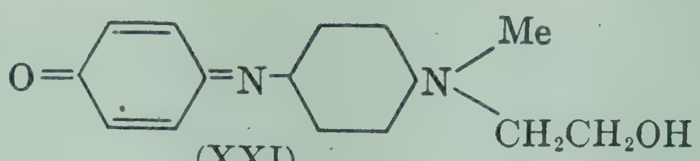

(XXI)

Greener blues are obtained from a naphthalene intermediate. Aqueous sulfurization of the leucoindophenol from mixed Cleve acids and *p*-aminophenol gives Immedial Green-Blue CV; using Cleve-6-acid, the product is Immedial Chrome Blue.[7] Immedial Indogen RCL is from (XXIV).[6] The product of the thionation of 1,5-dinitronaphthalene in presence of zinc chloride was marketed at one time as Melanogen Blue (MLB; CI 965). The dye may also be prepared by thionating the intermediate (probably XXII) for Naphthazarin, obtained by dissolving dinitronaphthalene in warm concentrated sulfuric acid, treating with hydrogen sulfide or a metal sulfide, diluting and precipitating with zinc chloride. Melanogen Blue dyed greenish-blue shades, converted into a bluish black by aftertreatment with copper sulfate. Kryogene Blues (BASF; CI 964) were similar dyes made from a mixture of 1,5- and 1,8-dinitronaphthalene. Blue sulfur dyes applicable to wool as acid colors are obtained by fusing α-naphthylamine-4,8-disulfonic acid or 4,6,8-trisulfonic acid with sulfur and alkali.[56]

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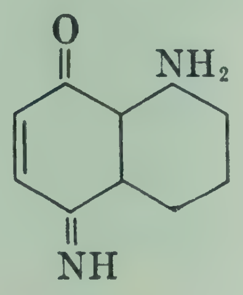
[54] *J. prakt. Chem.* **69,** 169 (1904).

[55] Cassella, DRP 199,963.

(XXII)



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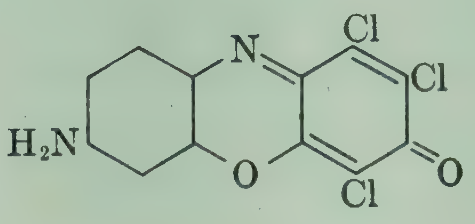


Immedial New Blue 5R, which gives "unusually bright and strong shades," is made by the thionation of the oxazone (XXIII).[8]

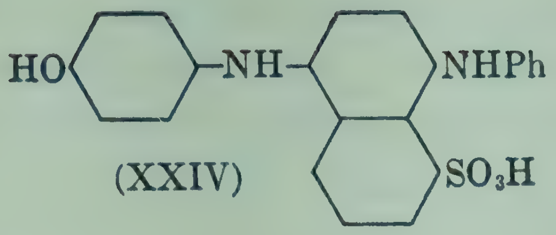
Green dyes are usually obtained by adding a copper salt to the thionation mixture, using suitable intermediates. Thus the thionation of *p*-aminophenol, which yields Vidal Black, gives Italian Green (CI 1002) by the action of aqueous sodium polysulfide and copper sulfate.[57] The shade changes to blue-black with weak oxidizing agents, and is destroyed by stronger oxidizing agents, so that it may be used in discharge printing. Immedial Dark Green B (IG) is made by refluxing *p*-nitrophenol with aqueous sodium polysulfide.[6] Eclipse Green G (GY) (Ris, 1901; CI 1004) is prepared from the sulfonic acid of the indophenol (IV), a green, instead of a blue, dye being obtained by the intervention of a copper salt. Particularly good fastness to light is claimed for the green dyes prepared by thionating indophenols containing an acylamido group.[58] Thionation of the indophenol from α-naphthylamine and *p*-aminophenol with aqueous sodium sulfide and copper gives Immedial Green G. Immedial Green BB (C) (Immedial Brilliant Green B, IG; Pyrogene Green G, Cb) (Böniger, 1904; CI 1006), which contains copper in combination with the organic molecule, is prepared by heating the leucoindophenol (XXIV; from *p*-aminophenol and phenyl-peri-acid) with sodium sulfide, sulfur and copper sulfate in aqueous solution.[59] Using a higher proportion of copper, a yellower brand (Immedial Green GG) is obtained; (XXIV) (200 kg.), sodium sulfide crystals (560), sulfur (208) and copper sulfate (40) are refluxed at 109° for 20 hours; after dilution, the dye is precipitated by air, filtered and dried. Using slightly different conditions of

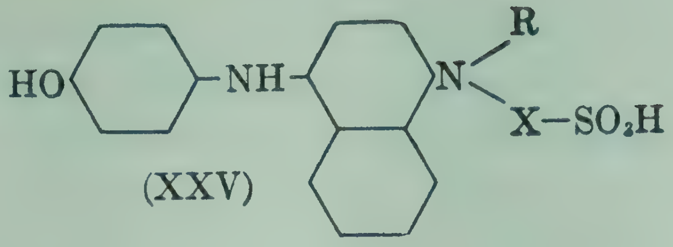
[56] Kalle, FP 471,230.

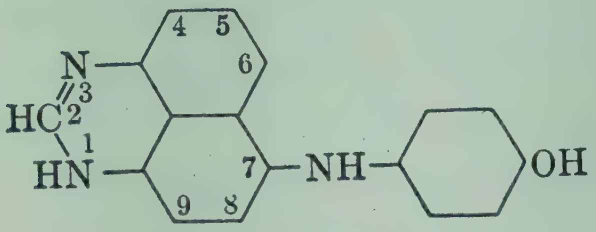
[57] Lepetit, Dollfus, and Gansser, DRP 101,577.

[58] IG, BP 504,835.

[59] Böniger and Sandoz, BP 11,863; USP 776,885.


(XXIV)


(XXV)


(XXVI)

thionation, Immedial Brilliant Green G (or Immedial Green GG extra) is produced.[7] The 5G brand is made from the tolyl analog of (XXIV).[6] Immedial Green 2B (IG) is made by a process similar to that used for Immedial Brilliant Green B, but copper sulfate is omitted.[6] Thionone Brilliant Green GG conc. (LBH), prepared from (XXIV) by boiling with aqueous sodium sulfide and copper powder (or copper sulfate) at 120° for 20 hours, has been stated to be "particularly fast to light and washing."[2] These are the most important of the sulfur greens. A bright green dye made by thionating the indophenol from *N*-*p*-acetamidophenyl-1-naphthylamine and *p*-aminophenol has better washing fastness than Immedial Green GG, and it was scheduled for manufacture by IG.[8]

Indophenols from 1-naphthylamine-6-, 7-, and 8-sulfonamides, carboxyphenyl-1-naphthylamine, and *p*-hydroxyethoxyphenyl-α-naphthylamine have been used for sulfurization, apparently with the object of improving solubility in the dyebath.[60] Blue to green sulfur dyes for wool and silk have been prepared[61] by thionating an ω-sulfoalkylamine of the type (XXV) in presence of a copper salt; R = H or alkyl, and $X = C_2H_4$, C_3H_6, etc.; the phenol residue may contain one or two halogen atoms.

The indophenol from 2-anilinoacridone and *p*-nitrosophenol gives a green dye with good light fastness.[62] Perimidine (1,3-*peri*-naphthodiazine) derivatives, such as (XXVI), give green dyes. Immedial Green BT extra is prepared by refluxing an ethanol solution of (XXVI) (230 kg. of 31.5% aqueous paste), sodium sulfide conc. (75) and sulfur (72) for 60 hours; ethanol is distilled off and the residue is heated at 102–103° for 12 hours. Immedial Green MK extra is prepared similarly from the 2-methyl derivative of (XXVI).[7] Both these dyes were made by IG on a small scale.

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[60] du Pont, USP 2,344,625; Chapman, Waddington and ICI, BP 406,280; IG, BP 490,067.

[61] Bigelow and du Pont, USP 2,335,381.

[62] IG, FP 892,409.

Thionation of the indophenol from 1-amino-5-naphthol and *p*-aminophenol with sodium polysulfide solution gives a gray dye, Immedial Fast Field Grey B.[7] Sodium polysulfide fusion of 3,5,8,10-tetrachloropyrene-1,6-quinone gives a greenish-gray dye useful for dyeing uniforms.[8]

Black dyes. The earlier sulfur blacks, such as Vidal Black FF from *p*-aminophenol and Immedial Black FF extra (Immedial Black V extra, IG) from 2,4-dinitro-4′-hydroxydiphenylamine, have been more or less completely displaced at the present time by the cheaper and faster black obtained by the thionation of 2,4-dinitrophenol.[63] This dye, Sulfur Black T (CI 978) (Immedial Black NN; Thionol Black, Pyrogene Deep Black; etc.) is made by all the leading dye manufacturers, and sold in many different brands, varying in the tone of the black and the physical form of the dye. Sulfur Black is not merely the most important sulfur color, but considering the quantities produced (over 10000 tons a year) it is the most important single dye of any class; in the United States figures for 1941 it represented over 10% of the total tonnage of the thousand or more dyes produced. The commercial importance of the dye is due to its ease of preparation, cheapness, and dyeing and fastness properties. Full black shades are obtained on cotton by air oxidation after dyeing in the usual manner from a sodium sulfide bath, and they have been stated to be "remarkably fast to light, acids, alkalis, scouring and milling"; this is broadly true, the fastness to light being 7, and the fastness to other agencies except chlorine being of the order of 4–5. The chlorine fastness is poor as for other sulfide dyes. One disadvantage of some Sulfur Blacks is the tendency to develop sulfuric acid in storage or on the dyed material; as a result there is a danger of the tendering of the cotton fiber. Sulfur Black shades which have been aftertreated with copper salts for improving the brightness, and shades on cotton-wool unions which have been cross-dyed with acid colors, are particularly susceptible to the oxidation and tendering action. Methods have been suggested (e.g., aftertreatment with mild alkali) to avoid or minimize the action, but it would appear that it is the quality of the dye which matters, since it is possible to prepare Sulfur Blacks which are largely free from this defect.[64] Tendering of Sulfur Blacks may also be partly prevented by complete oxidation of the dyestuff in the interior of the fiber.

Although 2,4-dinitrophenol, sodium sulfide and sulfur are used in the manufacture of the various brands of the Sulfur Black T type of dye, the products are chemically by no means identical; the constitution (as yet undetermined) and the composition (including the sulfur content) are variable in accordance with the conditions employed for thionation. Rowe[65] has suggested that the probable mechanism of the reaction involves the formation of 4-nitro-2-aminophenol which may immediately condense with sulfur or undergo further reduction to the diamine, since different products are obtained by starting with 4-nitro-2-aminophenol or 2,4-diaminophenol. Dinitrophenol is prepared by the hydrolysis of 2,4-dinitrochlorobenzene (free from water and acid; setting point above 47°) with boiling caustic soda solution; the product may be employed for thionation without isolating the phenol; the chloro compound may also be used directly by treatment with a mixture of aqueous caustic soda, sodium sulfide and sulfur. Typical conditions for the thionation are as follows: (a) heat dinitrophenol (1 part) with sodium sulfide (2) at 140° until reduction is complete; add sulfur (1) and sodium sulfide (2.5) and heat to dryness at 140°; (b) boil a solution of dinitrophenol (30), crystalline sodium sulfide (125) and sulfur (45) in water (150) under reflux (103–106°) for 25–40 hours; (c) heat an aqueous solution as above, but under pressure at about 160°. Pressure sulfurization effects a shortening of the time and a slight saving in steam and sulfur; but Sulfur Blacks of equally good quality can be produced by thionation at atmospheric pressure. Shade variations towards redder or greener blacks (e.g., various brands of Immedial Black, such as AWL extra, ML extra strong, MO, MOR, MORR extra strong) are obtained by adjusting the conditions of thionation and by the addition of picramic acid, dinitrocresols, β-naphthol, etc. Thus picric acid is added for redder blacks. The dye is isolated by air oxidation, and it may be purified by redissolving in aqueous sodium sulfide and reprecipitating. For producing the dye in a readily soluble form and for standardization, a solution of the dye in aqueous sodium sulfide is dried on a double drum dryer. Production of Sulfur Black by continuous passage of a mixture of dinitrophenol, sulfur and an aqueous solution of caustic soda and sodium sulfide through a reaction zone in which it is exposed for 10–15 minutes to a temperature of 150–160° has been claimed.[66]

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[63] AGFA, DRP 127,312; 127,835; Sandoz, DRP 136,016; StD, DRP 218,517; Vidal, BP 141,759.

[64] Whittaker and Wilcock, Dyeing with Coal-tar Dyestuffs, 5th ed., Bailliere, Tindall and Cox, London, 1949.

A Sulfur Black with improved exhaust properties is obtained by suspending the dye in water containing 0.1 to 1 part of an alkali cyanide or thiocyanate at pH 8 to 9.5, and aerating at a temperature above 65°.[67] Condensation of reduced Immedial Blacks (from di- or trinitrophenol) with formaldehyde introduces $-SCH_2OH$ groups; and the products are relatively nontendering.[8]

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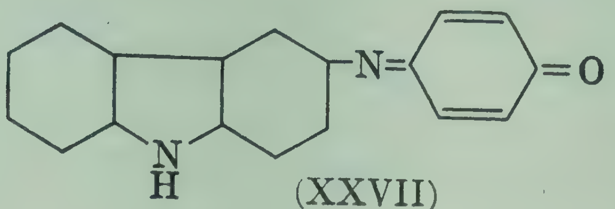
[65] *J. Soc. Dyers Colourists* **33,** 9 (1917).

[66] Kuznetsov, Silin, and Agaltsov, RP 67,125.

[67] Bigelow, USP 2,418,816.

Black sulfur dyes have also been prepared from the dinitronaphthalenes and the dinitroanthraquinones.

When carbazole-indophenol (XXVII) (see Chapter XXXVI under Hydron Blue) is thionated by means of sodium polysulfide and copper sulfate in butanol solution under reflux, a black sulfur dye, Indocarbon SN, which has better fastness to chlorine (grade 3) than Sulfur Black T is obtained.[68] Indocarbon CL is made by the sulfurization of *N*-*p*-hydroxyphenyl-β-naphthylamine (XXVIII), mixed with about 2.6% of 4,4′-dihydroxydiphenylamine and 5% of phenol, with sodium sulfide and sulfur in boiling butanol. Indocarbon CLG is prepared by heating (XXVIII) (90 parts), *p*-nitrophenol (6), *m*-toluylenediamine (4), caustic soda (89) and sulfur (196) in butanol (450) under reflux (110°) for 30 hours. Sodium nitrite (90) is then added, and the mixture again refluxed for 1–2 hours, diluted with water, and steam-distilled to remove the solvent. After separating the dye in a filter-press, the press-cake is taken up in water (200) and acidified with concentrated hydrochloric acid (50) at 60°. The dye is filtered, washed and dried *in vacuo;* the yield is 341 parts. Similar dyes (Indocarbon CL fine for printing; Indocarbon IB for printing) are obtained by thionating a mixture of (XXVII), (XXVIII) and a small amount of *m*-toluylenediamine. Brilliant Indocarbon CLB is made by thionation of a mixture of (XXVII) (8), (XXVIII) (64) and *p*-nitrophenol (8) with caustic soda (70) and sulfur (157) in boiling butanol; the product is worked up like Indocarbon CLG.[6]



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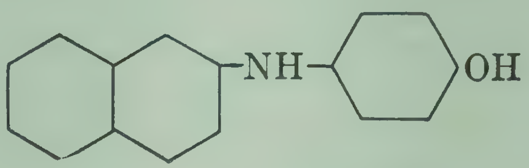

(XXVIII)

PROPERTIES OF SULFUR DYES

The storage of sulfur dyes calls for care; closed vessels and cool, dry conditions are essential. Even when these precautions are taken, they cannot be stored indefinitely, since gradual deterioration is liable to occur. Samples have therefore to be submitted to estimation by dye-trial before use.

Although the sulfur dyes are prepared from varied types of intermediates and under varied conditions, their chemical reactivity and dyeing properties are very similar, being essentially dependent on their containing sulfur as sulfide or disulfide linkages or thiazole or thiazine ring systems. Sulfur dyes by definition are soluble in aqueous sodium sulfide, usually forming colloidal solutions. On reoxidation, usually by atmospheric oxygen, the dyes are regenerated. They are insoluble in water, dilute acids, and the common organic solvents. Commercial dyes may contain water-soluble and alkali-soluble constituents.[69] A sample of a sulfur dye may have some solubility in water because of incomplete oxidation, mercapto groups, and the presence of alkali or sodium sulfide. Dyes containing free amino groups may be acid-soluble and can then dye wool like the basic dyes.

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[68] Ballauf, Muth, Schmelzer and Bayer, DRP 422,168; Ballauf, Muth, Schmelzer, and IG, DRP 431,221; Merte and Kalle, DRP 432,177; Maximilian, Schmidt, Merte, and Kalle, DRP 450,864.

Many sulfur dyes dissolve in concentrated sulfuric acid, aqueous caustic soda, hot pyridine and hot aniline; and the characteristic colorations are sometimes useful in identifying the dyes and in detecting mixtures. In examining the solubility of sulfur dyes, particularly in nitrobenzene, aniline, pyridine and similar solvents, it is necessary to remember the possibility of interaction between dye and solvent. This is also true of treatment with inorganic reagents such as acids, alkalis and alkali sulfite, sulfide, and hydrosulfite. Even with treatments in which the dye can be later recovered, the soluble substance is probably a derivative or fission product of the dye. Reduction (e.g., of the dyes derived from diphenylamine) with zinc and acetic acid, or stannous chloride and hydrochloric acid, often results in degradation, indicated by evolution of hydrogen sulfide. Alkaline reducing agents may liberate ammonia and effect a profound alteration in the constitution of the dyes. When the product of alkaline reduction is acidified, large amounts of hydrogen sulfide are evolved; with purified Sulfur Black for instance, nearly half the sulfur content can be accounted for in this manner by absorbing the hydrogen sulfide in excess of standard iodine solution. Sulfur dyes are readily attacked by chlorine, fuming nitric acid, dichromate and other oxidizing agents, with the formation of oxygenated products, sulfur dioxide, sulfur trioxide or sulfates, depending on the conditions of the treatment.

The sulfur dyes are amorphous, and the X-ray diffraction photographs are characteristic of non-crystalline substances.[70, 71] Perhaps the only sulfur dye to be obtained crystalline is Thiophor Indigo (Carl Jager)[2] which is prepared by the thionation of the indophenol (XXIX) and is stated to crystallize from benzene in small prisms with a coppery

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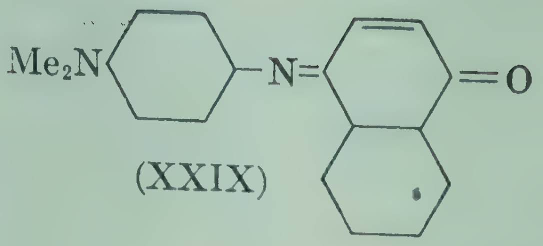
[69] Cf. Khailov and Ivanova, *Khlopchatobumazhnaya Prom.* **7,** No. 11, 46 (1937).

[70] Fierz-David *et al.*, *Helv. Chim. Acta* **15,** 287 (1932); *ibid.* **16,** 585 (1933); *J. Soc. Dyers Colourists* **51,** 50 (1935); *Naturwissenschaften* **20,** 945–7 (1932).

[71] Jones and Reid, *JACS* **54,** 4397 (1932), *et seq.*



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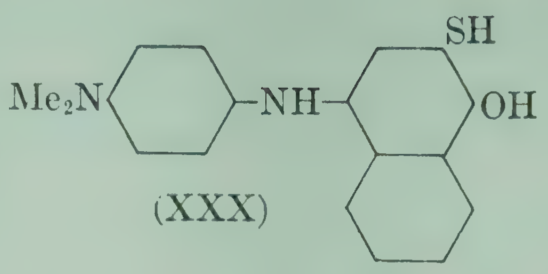

(XXX)

luster. In view of the dye possessing the indophenol character of ready hydrolysis with acids, the leuco derivative of the dye was assigned the constitution (XXX). Unlike most of the sulfur dyes, Thiophor Indigo is soluble in organic solvents such as ether. The solution in aqueous sodium sulfide is pale greenish yellow.

Although dye manufacturing processes are controlled and standardized in order to produce homogeneous dyestuffs with specific dyeing properties, the nature of the thionation process indicates that a sulfur dye is likely to consist of a mixture of compounds, varying in molecular size, sulfur content and other properties. The formation of mixtures in sulfurization has been demonstrated by Jones and Reid,[71] and by Fierz-David and Bernasconi.[70] The former took great care to ensure that time, temperature and the other conditions of sulfurization were identical for each batch; but the sulfur content for the dyes obtained from separate batches varied to the extent of 3–12%. The latter authors examined three samples of Pyrogene Indigo: (1) from the melt of the manufacturers; (2) finished in the same plant; and (3) a similar French product, Immedial Indone JBN. After careful purification, the molecular formulas obtained were (1) $C_{36}H_{20}N_4S_5O_3$, (2) $C_{36}H_{20}N_4S_5O_5$, and (3) $C_{36}H_{22}N_4S_3O_5$. So far as commercial dyes are concerned, several are in fact prepared from a mixture of intermediates, and standardization is effected solely from the dyeing point of view. Their sparing solubility, tendency to interact with the reagents and solvents that may be used for purification, and noncrystallizability render them intractable for isolation as chemically pure individuals.

For some dyes, however, especially in the blue and green series, the conditions of sulfurization can be so standardized that the results are reproducible under identical experimental conditions. The products dye the same shade from fresh and standing baths and from the exhaust liquors. This led Fierz-David[70] to formulate a scheme for the purification of these dyes, the impurities being removed by exhaustive extraction, successively with dilute hydrochloric acid, dilute ammonia, water, alcohol, and ether. A few blue and green dyes such as Pyrogene Indigo, Immedial Pure Blue, Immedial Indone, and Hydron Blue have thus been purified; but molecular weights have not been determined and the homogeneity of the compounds was not assessed by chromatographic or other methods. In spite of the inevitable limitations of the procedure, Fierz-David has been able to assign structures to these dyes which largely explain their known properties. There are many sulfur dyes (e.g. Sulfur Black) which are not amenable to Fierz-David's purification process, because after a certain stage of purification they form colloidal solutions and cannot be extracted any further; and Fierz-David has observed that, in general, his method is inapplicable to sulfur dyes other than blues and greens.

Estimation of sulfur dyes. Difficulties in the purification of sulfur dyes and the indeterminability of their chemical constitution indicate that sulfur dyes cannot be estimated by chemical analysis. The usual method of assaying sulfur dyes is by dyetrials in comparison with standard samples. If the dye can be separated from extraneous matter such as free sulfur and inorganic salts by extraction methods, and the nitrogen and sulfur contents of the dye are determined, other samples of the dye which are assumed to contain the same homogeneous tinctorial constituent may be estimated by carrying out a dyeing on cotton yarn so as to exhaust the dyebath completely, washing the yarn thoroughly, and then determining the sulfur and nitrogen content of the yarn.[72] Apart from the intermediates which might have escaped thionation altogether and are in fact very unlikely to be present, the substances commonly occurring in sulfur dyes as impurities or as additions made during standardization are free sulfur and sodium sulfide, sulfate, thiosulfate, chloride, and carbonate, together with organic sulfur compounds representing intermediate stages of thionation as distinct from the essential coloring matter. The "pure dye content" of commercial sulfur dyes has been estimated[73] by electrolyzing a solution of the dye in aqueous sodium sulfite until oxidation is complete, and weighing the precipitated dye; platinum electrodes and a current of 3 amps for 30–75 minutes were found to be suitable. Precipitation of the dye from aqueous sodium sulfide solution by means of a basic dye, washing the precipitate in a specified manner, and weighing the precipitate, and colorimetric methods based on air oxidation of the aqueous sodium sulfide solution until the color intensity reaches a maximum, have been suggested.[74]

APPLICATION OF SULFUR DYES

Sulfur dyes are readily soluble in hot aqueous sodium sulfide, and the solutions have high substantivity for cotton. The formation of a leuco derivative or an addition compound with sodium sulfide is necessary for the dyeing process. Crystalline sodium sulfide (Na_2S, $9H_2O$) or the concentrated or "rock" brand of the sulfide which has twice the sodium sulfide content may be used, and soda ash may be added for the removal of lime salts. A large excess of sodium sulfide will retard exhaustion. Dyeing is carried out at the boil, but lower temperatures (about 60°) are recommended for a few blue and green dyes. Depending on the depth of the shade, 5–40% of common salt or twice this amount of Glauber salt, calculated on the weight of the cotton, is used for increasing and accelerating the absorption of the dye. The dyed material is then rinsed thoroughly; the final rinse for a few yellow and brown shades is carried out with very weak (about 0.02%) acetic acid. No further treatment is usually necessary, but various aftertreatments are sometimes employed. Sulfur dye shades are mostly dull; and hot soaping, adding oil emulsions if desired, has the effect of brightening the shades and softening the yarn. Blacks are aftertreated with sodium acetate or formate solutions to minimize the danger of tendering. Steaming in presence of air, or aftertreatment with sodium perborate or hydrogen peroxide, imparts a brighter and redder tone to the sulfur blues, but the fastness to washing is apt to be impaired. Fastness to light, washing and acid cross-dyeing is improved by aftertreatment with dichromate and copper sulfate; subsequent change of shade by slow atmospheric oxidation of the dyed fiber is also thus avoided. An interesting method of aftertreatment is to top with basic colors for which the sulfur dyes act as mordants; brighter shades with better fastness to washing are thus obtained.

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[72] Cf. Osipov, *Izvest. Tekstil. Prom. Torgov.* **10,** No. 12, 68 (1931).

[73] Smirnov, *Anilinokras. Prom.* **2,** No. 10, 28 (1932).

[74] Touschkof-Vtorov, *Rev. gén. mat. color* **33,** 313 (1929); Belenkii, *Melliand Textilber.* **14,** 555 (1933).

Except the blacks which are used for their cheapness, sulfur dyes are generally unsuitable for viscose, since unlevel shades are liable to be produced.

Sodium sulfide solutions of sulfide dyes are too strongly alkaline to be applied to wool by the ordinary dyeing process for cotton, and the use of sulfide dyes is largely limited to the dyeing of cellulose fibers. In the Lodge-Evans process for dyeing wool, sulfur dyes soluble in aqueous alkali sulfites are chosen; the sulfite solution of the dye is then reduced with the minimum amount of sodium sulfide in presence of neutral ammonium salts, so that the dyebath is practically neutral and does not damage wool.

The Immedialsols (IG) are mixtures of sulfur dyes with Rongalite, soda ash and a little lubricating oil.[8, 75] These dissolve readily in boiling water and give level dyeings, particularly on Zellwolle, a German rayon made from wood. Twelve Immedialsols were marketed, and they were recommended for use on staple fiber, cotton-wool unions, and casein fiber. Similar Swiss compositions of sulfur dyes have been on the

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[75] *BIOS* Misc. Report **20,** Appendix 85. Cf. IG, DRP 651,666; USP 2,055,746.

market. Thionol "M" dyes (ICI) are water-soluble sulfur dyes, giving clear solutions suitable for dyeing cotton in circulating liquor machines, but the addition of sodium sulfide and soda ash is necessary to convert the dissolved dye into a product possessing affinity for the cotton fiber.

Fastness properties. Sulfur dyes as a class exhibit better fastness to light, washing and acid cross-dyeing than many direct cotton dyes. The yellows, oranges and browns (except for a few of the dark browns) have moderate light fastness (3–4); the blues and greens have a light fastness grade of 5–6; and the blacks have excellent light fastness (7). The fastness to washing is uniformly high (4–5). Their main weakness is poor fastness to chlorine, which makes them valueless for materials to be bleached. It has been suggested that the fastness of sulfur dyes to chlorine can be increased by treatment with a melamine-formaldehyde resin, which forms a chloramine derivative with chlorine.[76]

CONSTITUTION OF SULFUR DYES

Attempts to determine the constitution of the sulfur colors have so far had only limited success, because of the intrinsic difficulties of the problem. The work of Fierz-David and others[70] has given us valuable data regarding the types of linkages and ring systems occurring in sulfur dyes and a broad correlation of such structural features with the color of the dyes; but it is doubtful if the usual chemical modes of attack will carry us much further, unless they are supplemented by physical methods. The colloidal nature of the solutions in sodium sulfide and other properties of the sulfur dyes indicate that many of them have large molecular weights, the sulfur atoms linking up smaller units to form high polymers.

In the sulfurization of organic compounds, sulfur enters the molecule in open chain linkages and/or heterocyclic systems. Sulfur in the side chain, which is often the major part of the total sulfur in sulfur dyes, may be present as mercapto, sulfide, disulfide, polysulfide, sulfoxide, and disulfoxide groups. The ring systems which have been identified with some certainty are thiazole in yellow and brown dyes, and thiazine in blue, green and black dyes. Other ring systems such as 1,4-dithiin, 1,4-thioxin and 1,2,5-thiadiazole have been postulated; but conclusive evidence has not been obtained. In addition to these the sulfur dyes naturally contain the cyclic skeletons (carbazole, azine, etc.) which are present in the intermediates used for thionation.

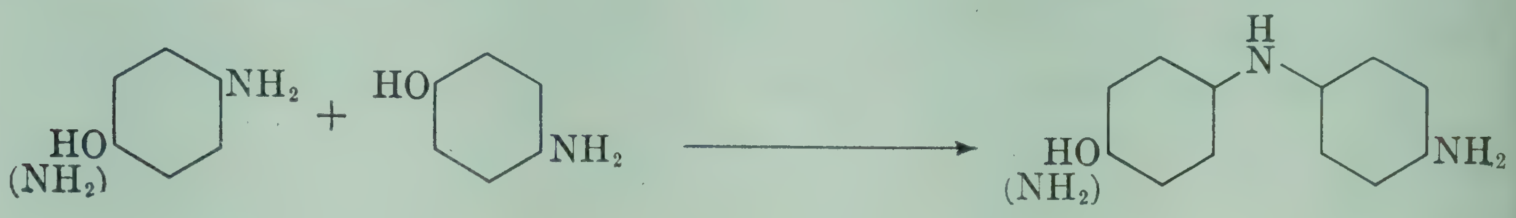
Mechanism of the formation of sulfur dyes. Vidal's pioneering work related not only to the technical production of black sulfur dyes, but also included a careful investigation of the mechanism of their formation.[65] He regarded the conversion of *p*-phenylenediamine and *p*-aminophenol

[76] Landolt, *Textil Rundschau* **11,** 201 (1947).

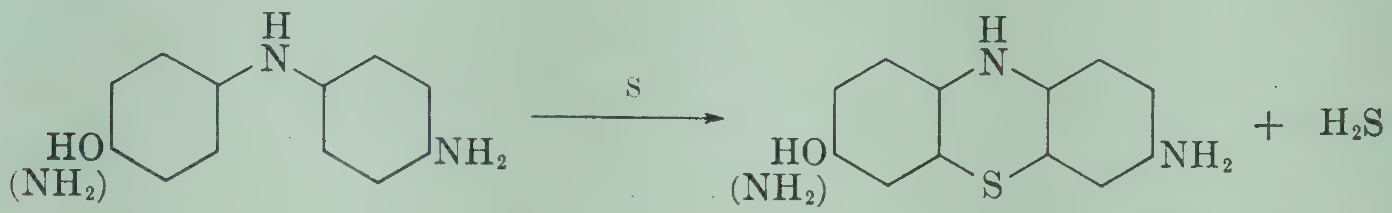
CHART 1

FORMATION OF BLACK DYES FROM DIPHENYLAMINE DERIVATIVES (VIDAL)

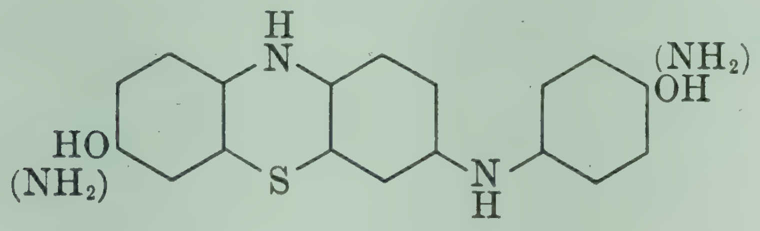
I Diphenylamine formation:



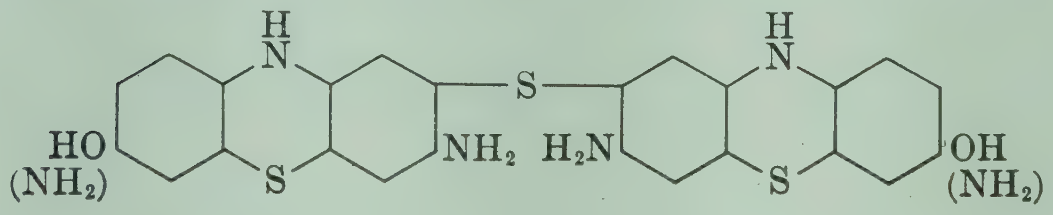
II Thiodiphenylamine formation.



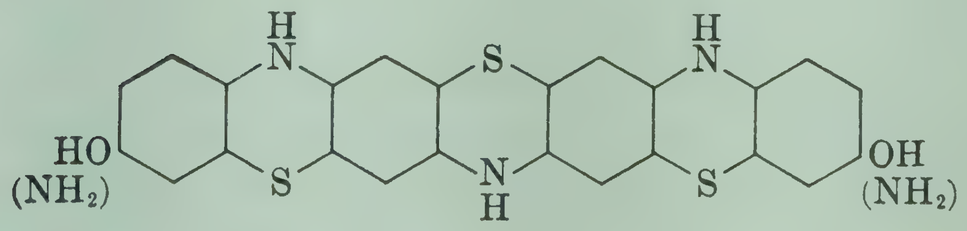
III (a) Thiodiphenylamine derivative:



(b) Blue dyestuff formation (without liberation of ammonia):



(c) Black dyestuff formation (with liberation of ammonia):



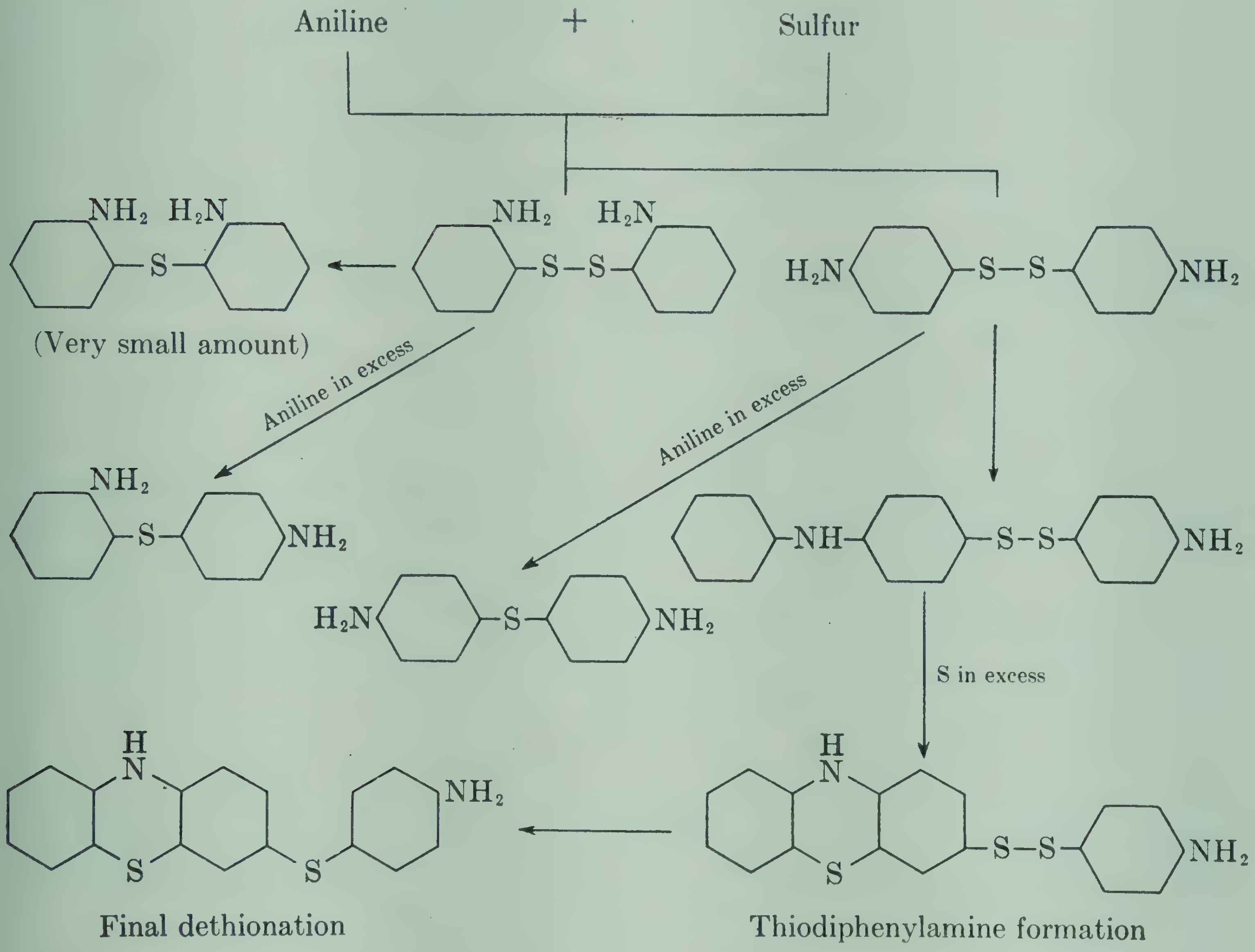
to diphenylamine derivatives as the first stage, confirmed by the formation of similar dyes when the latter were used as starting materials; and he postulated three stages in the conversion of diphenylamine derivatives to black dyes.

When aniline is heated with sulfur, a series of products are formed; the final thiodiphenylamine derivative is green in color, and Hodgson has obtained evidence for representing the reactions by the scheme shown in Chart 2.[77]

As the result of a study of the decomposition of Sulfur Blacks on keeping (spontaneous heating; formation of sulfuric acid; decrease in sodium sulfide solubility; lowered tinctorial power), Perret has suggested that Sulfur Blacks do not contain thiazine rings, but complex polythiazine rings of the type (I), formed through the stages of reduction of dinitrophenol to the amine, introduction of a mercapto group *ortho* to an amino group, polysulfide chain formation, and liberation of ammonia.[78] Chains of the type of R—S—S_x—SH were probably also present; in either case sulfur could be detached from the chain by slow oxidation without a fundamental change in the main nucleus. If Sulfur Black is prepared from pure sodium 2,4-dinitrophenate and sodium tetrasulfide, the mother liquor yields nearly pure sodium thiosulfate on evaporation; two sulfur atoms of the tetrasulfide enter the dye molecule, and sodium disulfide oxidizes to thiosulfate ($Na_2S_2 \rightarrow Na_2S_2O_3$).

CHART 2

ACTION OF SULFUR ON ANILINE


Aniline
+
Sulfur
NH₂ H₂N
S
NH₂ H₂N
S—S
H₂N
S—S
NH₂
(Very small amount)
Aniline in excess
Aniline in excess
NH₂
S
NH₂
NH
S—S
NH₂
H₂N
S
NH₂
S in excess
H
N
S
S
NH₂
H
N
S
S—S
NH₂
Final dethionation
Thiodiphenylamine formation

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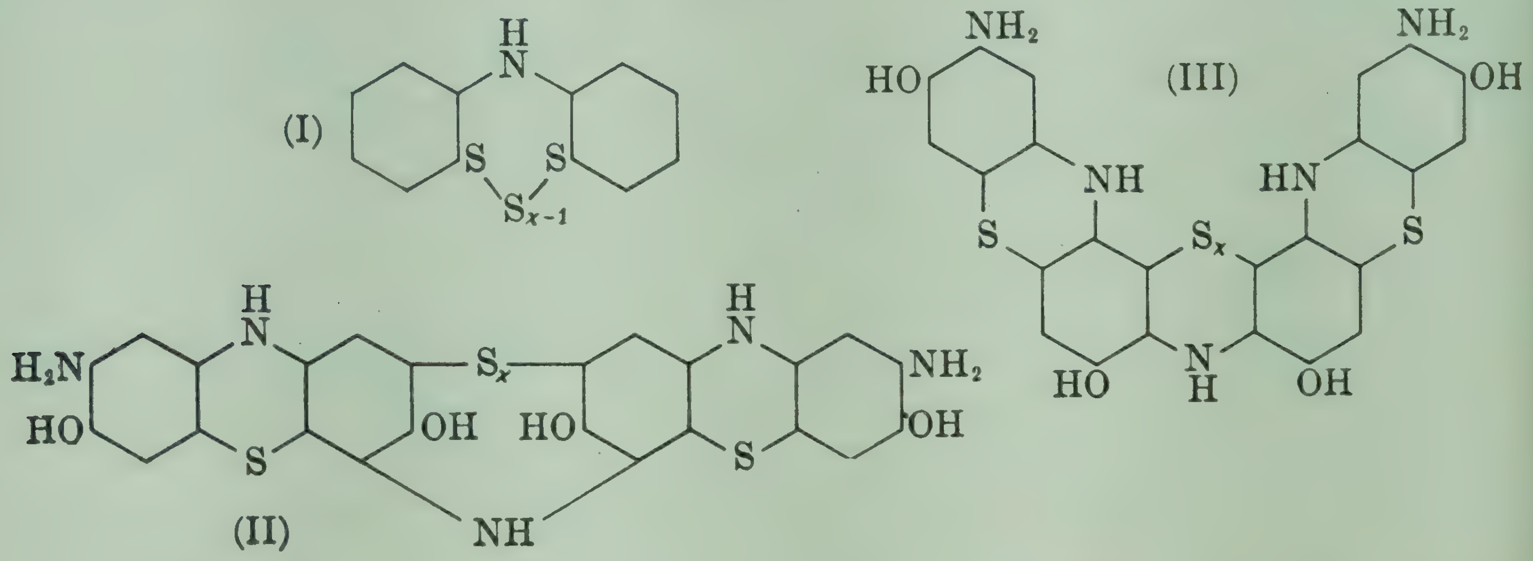
[77] Hodgson, *J. Soc. Dyers Colourists* **40,** 330 (1924); *ibid.* **42,** 76 (1926).

[78] *Ann. chim. applicata,* **16,** 69 (1926).

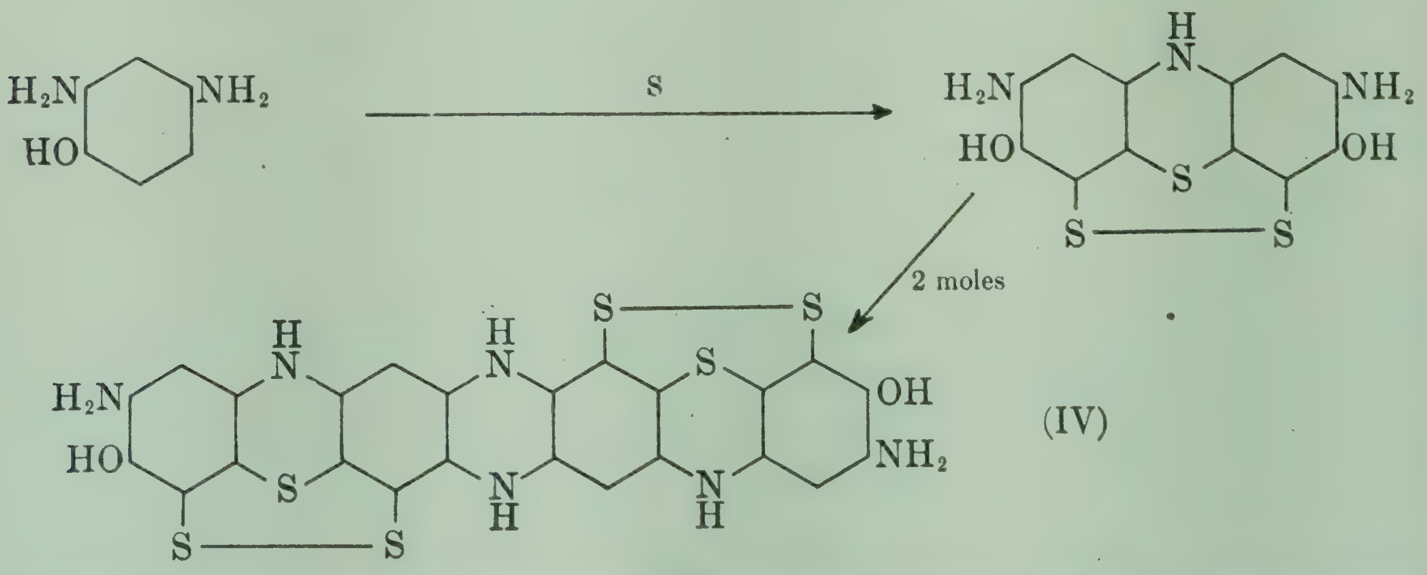
Kubota[79] treated 2,4-diaminophenol and 2,4-dinitrophenol with Na_2S_x at 140° for 5 to 90 hours, and found that the amount of combined sulfur was inversely proportional to the time of heating with preparations containing a large amount of sulfur. This was attributed to the decomposition of combined sulfur during heating. Dyes containing more than 30% combined sulfur led to greater deterioration of cotton fabrics. With dyes containing less than 20% combined sulfur deterioration of fibers was proportional to degree of heating. The constitution of black sulfur dyes derived from dinitrophenol was expressed as (II) and (III).


(I)

(III)

(II)

In the formation of a black dye from sodium dinitrophenate and sodium pentasulfide, reduction proceeds according to the equation: $Ar(NO_2)_2 + 2Na_2S_x + 2H_2O \rightarrow Ar(NH_2)_2 + 2Na_2S_2O_3 + 2S_{x-2}$, and is immediately followed by sulfurization, because the sulfur set free is in an active form.[80] A scheme, in which the constitution of Sulfur Black is pictured as (IV), has been proposed.[81]



(IV)

Fierz-David and Zucher explain the formation of a black dye by intense thionation of a bordeaux-red sulfur dye prepared from *p*-anisidine as follows:[70]

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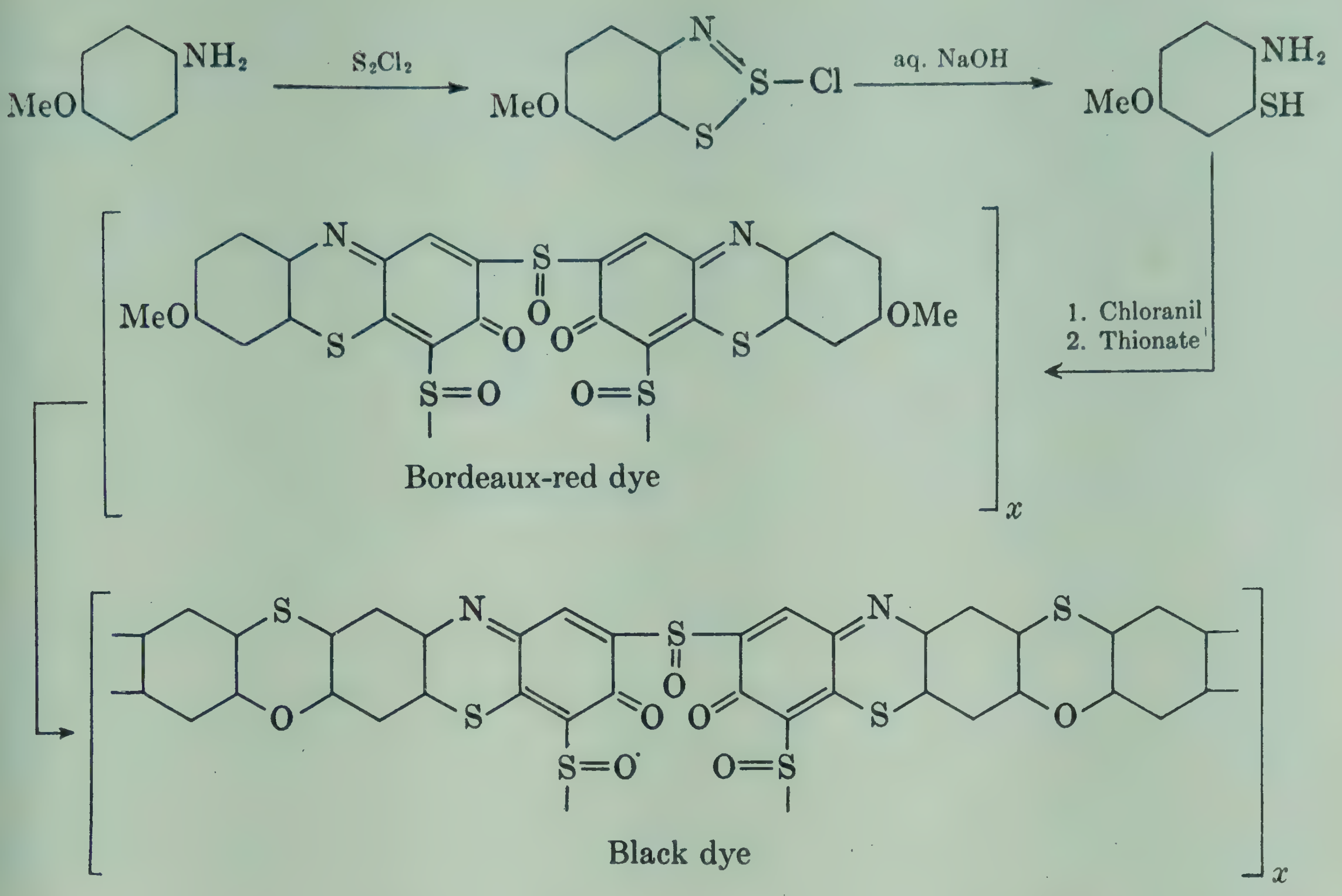
[79] *J. Chem. Soc. Japan* **55,** 565 (1934).

[80] Khmelnitzkaya and Verkhovskaya, *Anilinokras. Prom.* **2,** 31 (1932).

[81] *Anilinokras. Prom.* **5,** 67 (1935).



Bordeaux-red dye

Black dye

They studied the course of the reaction by determining the methoxyl content as sulfuration proceeded; the products turned blacker and the methoxyl content decreased, but the dyes could not be purified since they formed colloidal solutions. They assumed that thioxin rings were formed, replacing methoxyl groups.

Sulfur side chains. The existence of sulfur side chains has been well established. They are in the main nonchromophoric, and their influence is on the solubility of the dye in sodium sulfide and aqueous alkali, and partly on the dyeing and fastness properties. The position of the sulfur linkages is generally *ortho* to the amino or hydroxyl groups. When chlorinated intermediates are thionated, the halogen is usually replaced by sulfur; under suitable conditions of thionation, each chlorine atom can be replaced by a sulfhydric group, so that this provides a useful method for locating the position of the latter. Mercapto groups may occur as such, or they may be produced by reductive fission of disulfide linkages when the dye is dissolved in aqueous sodium sulfide; in either case their presence can be shown by the alkali solubility, alkylation to thioethers, and the formation of thioglycolic acid derivatives by condensation with chloroacetic acid. However, the presence of a disulfide linkage in a coloring matter is not enough to give it the dyeing properties of a sulfide dye.[82] The high proportion of sulfur in some sulfur dyes can only be explained on the basis of polysulfide chains. Möhlaus has pictured thionated phenol as (V) in which x may be as long as 8; and he has

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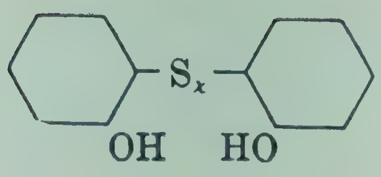
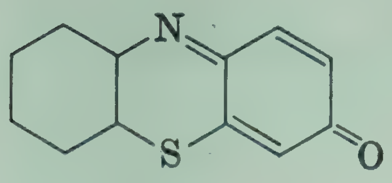
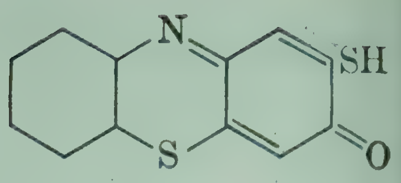
[82] Cf. Friedländer and Mauthner, *Z. Farb. Text. Ind.* **3**, 333 (1904).



(V)



(VI)



(VII)

suggested that in sulfur dyes containing thiazole and thiazine systems there may be polysulfide chains formed by attachment of extranuclear sulfur atoms to the ring sulfur.[83] In support of his postulate of polysulfide chains he cited the fact that it is possible to increase the chain length or molecular size of sulfur dyes without materially altering the color, but changing the solubility and other properties. Jones and Reid[71] substantiate the existence of polysulfide chains in sulfur dyes containing thiazine ring systems; when the compounds (VI) and (VII) are treated with stannous chloride and acid, hydrogen sulfide is not evolved; but the dyes lose as hydrogen sulfide all the sulfur other than the sulfur in the thiazine rings and the sulfur directly attached to the ring. The polysulfide bridges account for the large size of the molecules, the colloidal character, and many of the other properties.

Carbon-carbon linkage. From the products of the chlorination of a sulfur dye prepared from phenol, diphenyl 4,4′-disulfonyl chloride, m.p. 203°, has been isolated.[84] This would appear to be the only instance in which definite proof has been offered for the formation of carbon-carbon linkages in a thionation process, although Fierz-David has made this assumption in formulating a constitution for a black sulfur dye.

Ring systems in sulfur dyes. The constitution of dehydrothiotoluidine and Primuline,[85] clearly proved by the early work of Jacobsen and Gattermann, and the resemblance of many of the yellow, orange, and brown sulfur dyes to Primuline, have shown the presence of thiazole rings in these sulfur dyes. The thionation of amines (2,4-toluylenediamine, tolidine and similar compounds containing a carbon side-chain) proceeds like the formation of Primuline, and the products are colored insoluble substances containing thiazole ring systems. When these are solubilized by treatment with hot sodium sulfide solution, thiol groups are introduced and the true sulfide dyes are formed. The presence of dibenzothiophene rings, in addition to thiazole rings, has been assumed in the dyes formed by thionation of mixtures containing benzidine; the two ring systems can be in separate parts of the molecule or fused together as in (VIII). However, in Immedial Yellow GG, prepared by thionating benzidine and dehydrothiotoluidine, there appears to be no thiophene ring (see later).[86]

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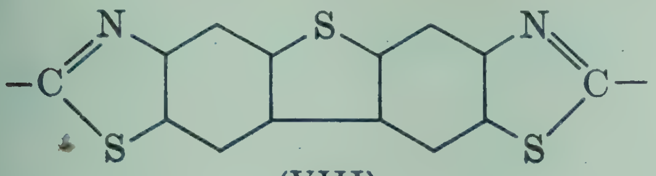
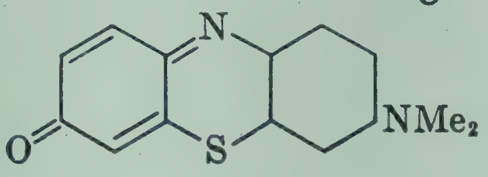
[83] Möhlaus and Seyde, *Chem-Ztg.* **31,** 937 (1907); Möhlaus, *Z. physik. Chem.* **54,** 274 (1906).

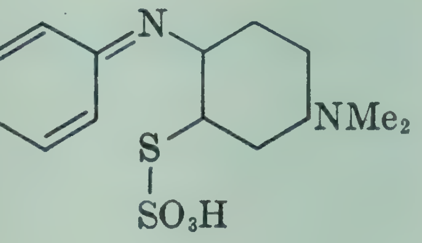
[84] Pollak, Riesz, and Nadel, *Montash.* **53-54,** 90 (1929).

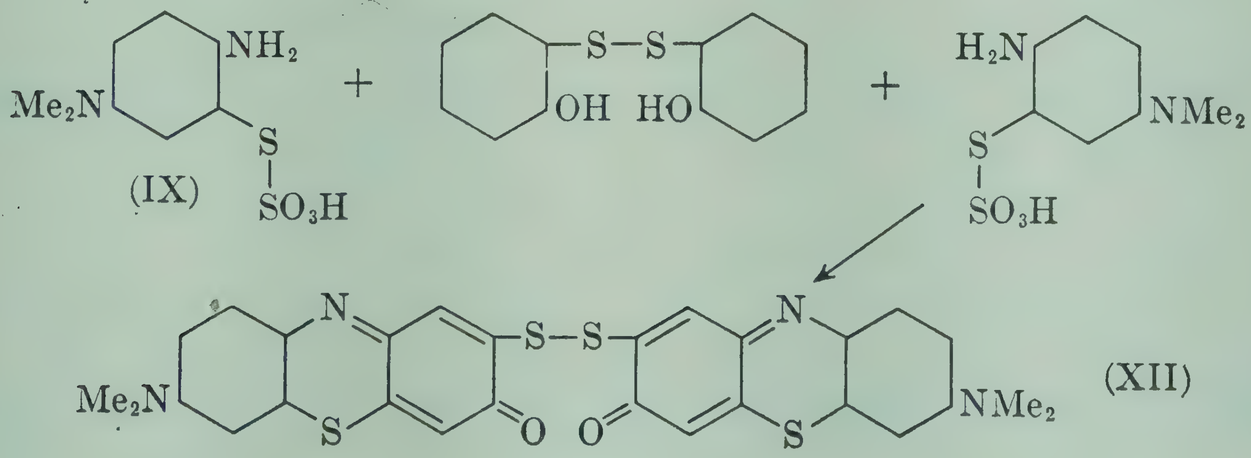
[85] Jacobsen, *Ber.* **22,** 330 (1889); Pfitzinger and Gattermann, *ibid.* 1063.

Since the constitution of Methylene Blue as a thiazine and the mechanism of its formation from the thiosulfonic acid (IX) were known, the fact that Methylene Blue and thiosulfonic acids analogous to (IX) could be converted into blue, green and black sulfur dyes by thionation processes provided preliminary evidence of the presence of thiazine rings in such dyes. Thiosulfonic acids prepared from certain indophenols and amines give the Methylene Blue type of blue and black dyes by oxidation with dichromate, and sulfur dyes of very similar shades by thionation; the difference is in the dyeing properties. Methylene Violet (X) and the indophenol-thiosulfonic acid (XI) yield on treatment with aqueous or alcoholic sodium tetrasulfide at about 140° a blue dye, similar in dyeing properties to Immedial Pure Blue. By the oxidation of (IX) together with 2,2′-dihydroxydiphenyldisulfide, Meyenberg and Levy obtained a blue sulfide dye (XII); in view of the known mechanism of the formation of Methylene Blue and other thiazine dyes, the reaction must take place as indicated.[87] When Immedial Pure Blue is heated in a sealed tube with potassium dichromate and hydrogen bromide, tetrabromo Methylene Violet (XIII) is obtained in 42% yield, and (XIII) has also been prepared from Methylene Blue.[88] Vidal's experiments on the mode of


(VIII)


(X)


(XI)


(IX)

(XII)

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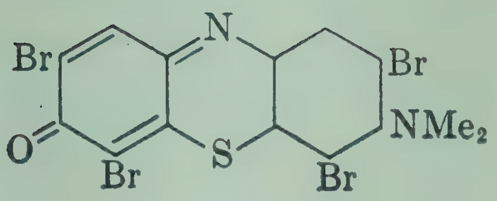
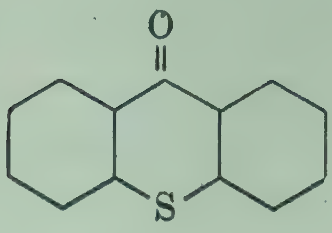
[86] Zerweck, Ritter and Schubert, *Angew. Chem.* **60A**, 141 (1948).

[87] *Rev. gén. mat. color.* 212 (1902).

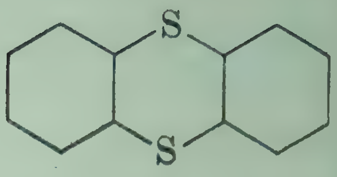
[88] Gnehm and Kaufler, *Ber.* **37**, 2618, 3032 (1904).



(XIII)



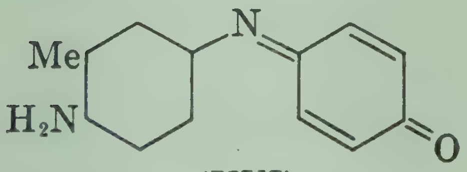
(XIV)



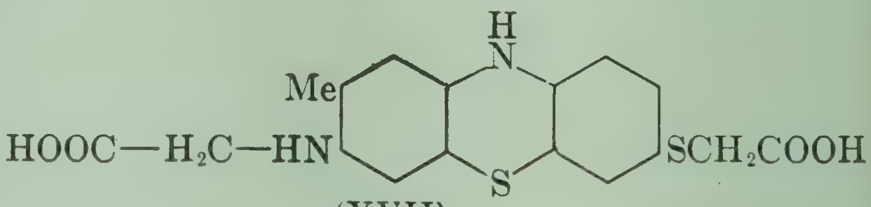
(XV)

formation of sulfur blues and blacks showed that diphenylamine derivatives were first converted into thiodiphenylamine derivatives. Jones and Reid[71] found that the bordeaux dyes prepared from *p*-hydroxydiphenylamine and its *p*′-methyl homolog contained thiazine rings as the fundamental structural units; they were very similar in properties to the red thiazone (VI) prepared by Bernthsen.[89]

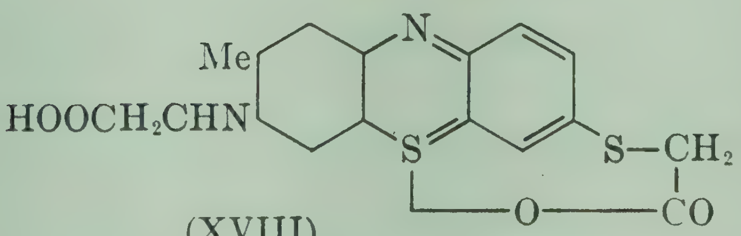
Sulfur dyes prepared from fluorescein and certain other intermediates are believed to contain thioxanthone rings (XIV); and dyes prepared from diphenylamine disulfide to contain thianthrene rings (XV).[65] A thianthrene derivative is produced by the action of sodium sulfide on 2,3-dichloro-1,4-naphthoquinone, and by analogy Zerweck, Ritter and Schubert have postulated the presence of thianthrene rings in dyes such as Indocarbon CL, Immedial Pure Blue and Hydron Blue, which are thionation products of indophenols. Such dyes can also be prepared by the further thionation of intermediates, which presumably contain the thianthrene ring system, since they are obtained by the action of sodium sulfide on condensation products of chloranil and an *o*-aminothiophenol.[86,89a] The experimental evidence for the thianthrene structure is discussed more fully in connection with Hydron Blue (see Chapter XXXVI).



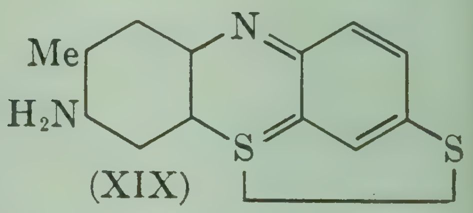
(XVI)



(XVII)



(XVIII)



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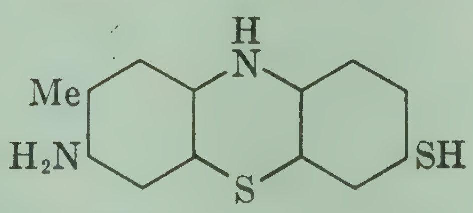

(XX)

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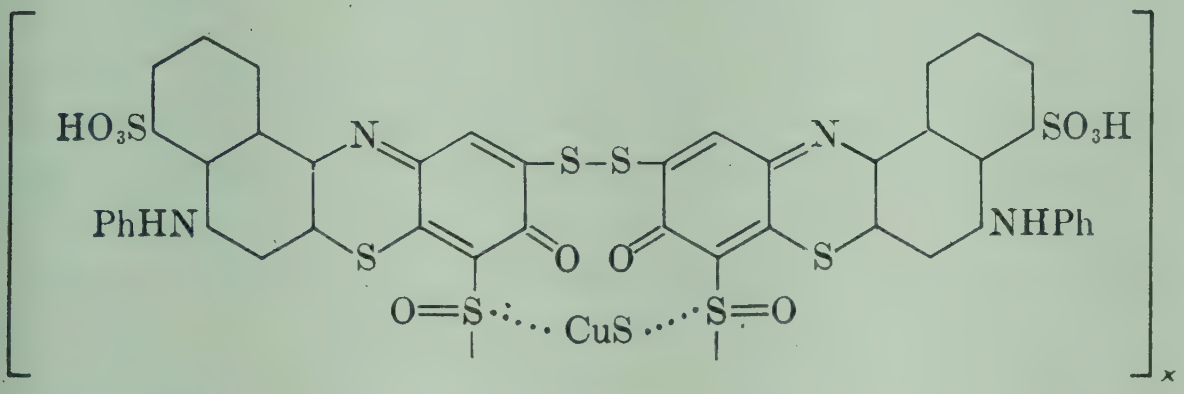
[89] *Ann.* **230,** 182 (1885); *Ber.* **17,** 2860 (1884).

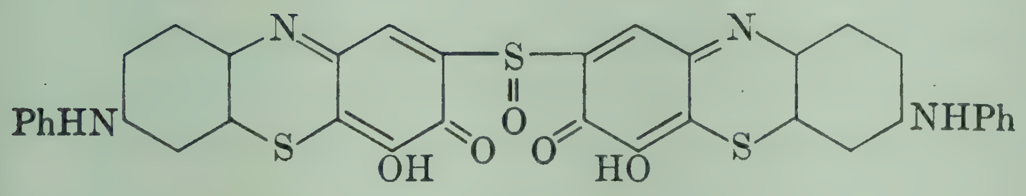
[89a] Brass and Köhler, *Ber.* **55,** 2543 (1923).

Structures assigned to individual sulfur dyes. Immedial Indone, prepared by the thionation of the indophenol (XVI), was found by Frank to condense with chloroacetic acid, forming a readily purified compound (XVII) containing two CH_2COOH groups.[90] This acid (XVII) gave on oxidation a blue dye, which dyed wool as an acid color and did not behave as a sulfide dye. The structure (XVIII) was assigned to the wool dye, and Immedial Indone and its leuco derivative were formulated as (XIX) and (XX).

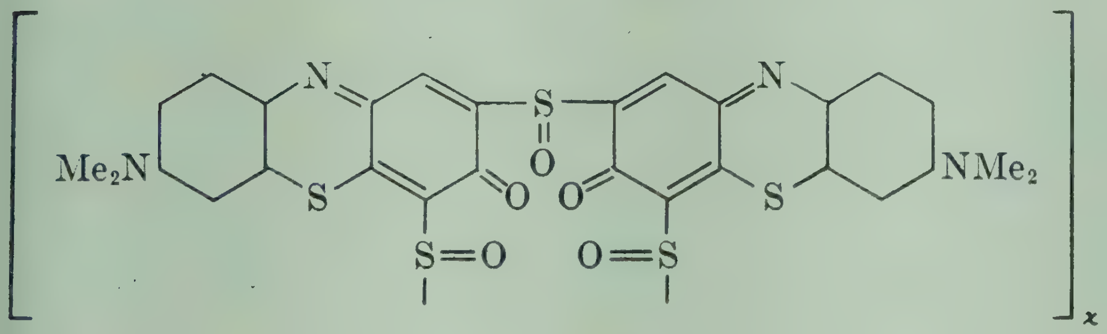
The structures proposed by Fierz-David and his collaborators[70] for Immedial Pure Blue, Pyrogene Indigo, Pyrogene Green and Immedial Indone JBN, as well as the sulfurized vat dyes Hydron Blue, Cibanone Yellow R and Cibanone Orange R (see Chapter XXXVI), have been mainly based on elementary analysis; spectroscopic evidence, of which details have not been stated, has been cited in a few cases. The thiazine units in Immedial Pure Blue, Pyrogene Green and Hydron Blue were estimated by sulfonating the dyes with a mixture of concentrated sulfuric acid and chlorosulfonic acid to make them water-soluble, and then



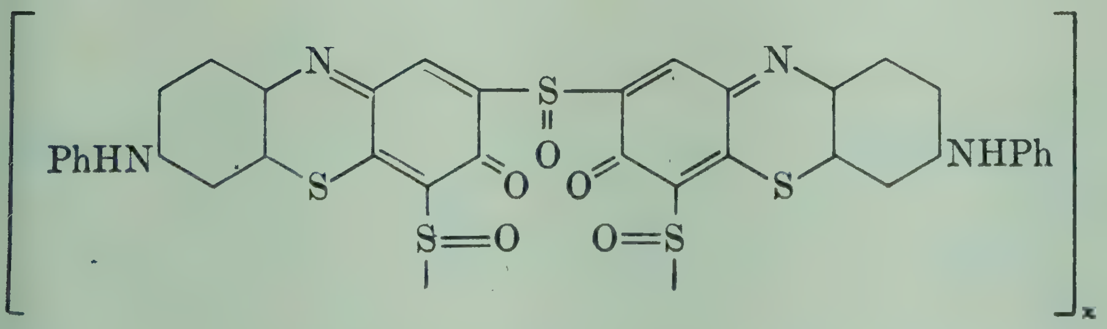
Pyrogene Green



Immedial Indone JBN



Immedial Pure Blue



Pyrogene Indigo

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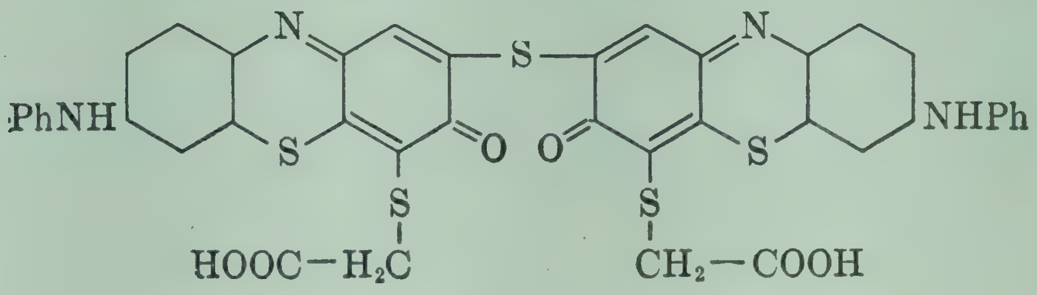
[90] Cf. Frank, *JCS* **97T, 2044** (1910).

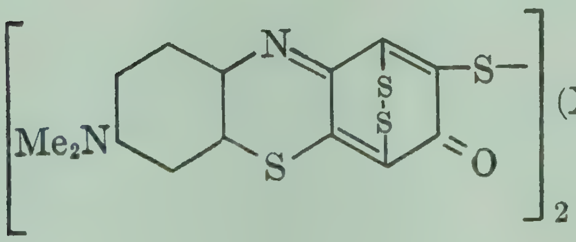
titrating them with titanous chloride. The possibility of the dyes decomposing during the acid treatment and the recorded results of the titrations indicate the limited value of this method. The condensation of the leuco derivative of Pyrogene Indigo with chloroacetic acid gave a compound formulated as (XXI), which was considered as confirming the presence of two disulfide (or disulfoxide) linkages per unit in the dye molecule; but the instability of the compound and the likelihood of the phenolic hydroxyls also reacting with chloroacetic acid render it necessary to interpret the results with caution. However, the qualitative evidence of the presence of thiazine ring systems is conclusive; the doubtful factors in Fierz-David's structures are mainly the number and nature of the extranuclear sulfur linkages. Further, seeing how readily diphenylamine cyclizes to thiodiphenylamine, the formation of thiazine rings involving the anilino groups in dyes such as Pyrogene Green has to be visualized.



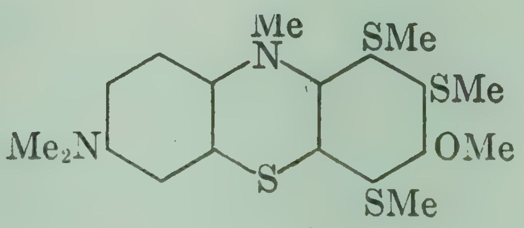
(XXI)

Keller and Fierz-David attribute the solubility of the Immedial Pure Blue type of dye in aqueous sodium sulfide to reduction of quinone groups and fission of disulfoxide groups. The colloidal properties show that they are polymers, the polymerization taking place probably through the sulfoxide groups. An inference of Keller and Fierz-David is that for these blue dyes (including the Hydron Blue type) the terminal amino groups must be substituted; primary amino groups lead to black dyes by formation of more complex thiazines.

For the Immedial Pure Blue type of sulfur blue,[91] Binz and Rath[92] propose the structure (XXII). They prepared the leuco derivative by dissolving the dye in aqueous sodium sulfide and precipitating by means of carbon dioxide and a little hydrochloric acid; this reacted readily with



(XXII)



(XXIII)

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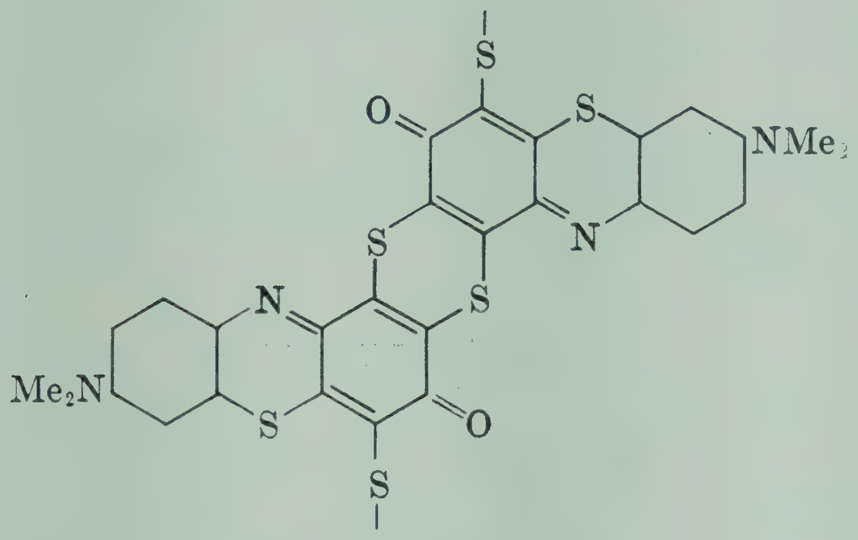
[91] BASF, DRP 167,012.

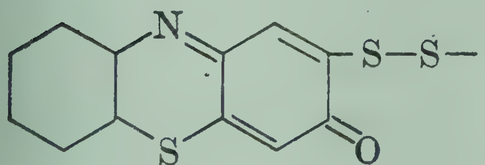
[92] *Ber*, **58B**, 309 (1925).

diazomethane in ether with copious evolution of nitrogen and the formation of a pentamethyl derivative agreeing in composition with (XXIII). Structure (XXII) may be compared with (XII) suggested many years earlier by Meyenberg and Levy for a blue sulfur dye.[87] External attachment of sulfur to dibenzothiazine units is more probable than the cage system in (XXII). Zerweck, Ritter and Schubert[86] suggest the following structure for Immedial Pure Blue, which is in conflict with the claim of Binz and Rath that they obtained (XXIII) by reduction of the dye and methylation.

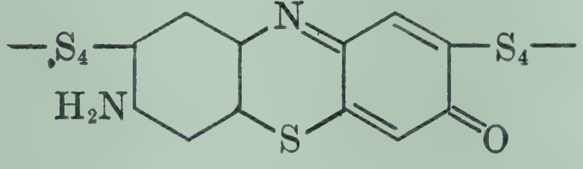


Immedial Pure Blue

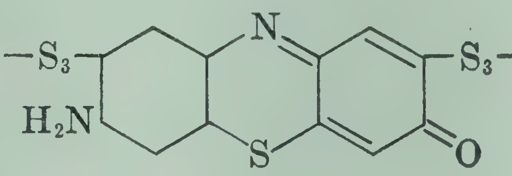
For the dyes prepared by treatment of diphenylamine derivatives with aqueous sodium polysulfide, Jones and Reid suggest thiazone structures linked by polysulfide chains, such as (XXIV) for a bordeaux-red



(XXIV)



(XXV)

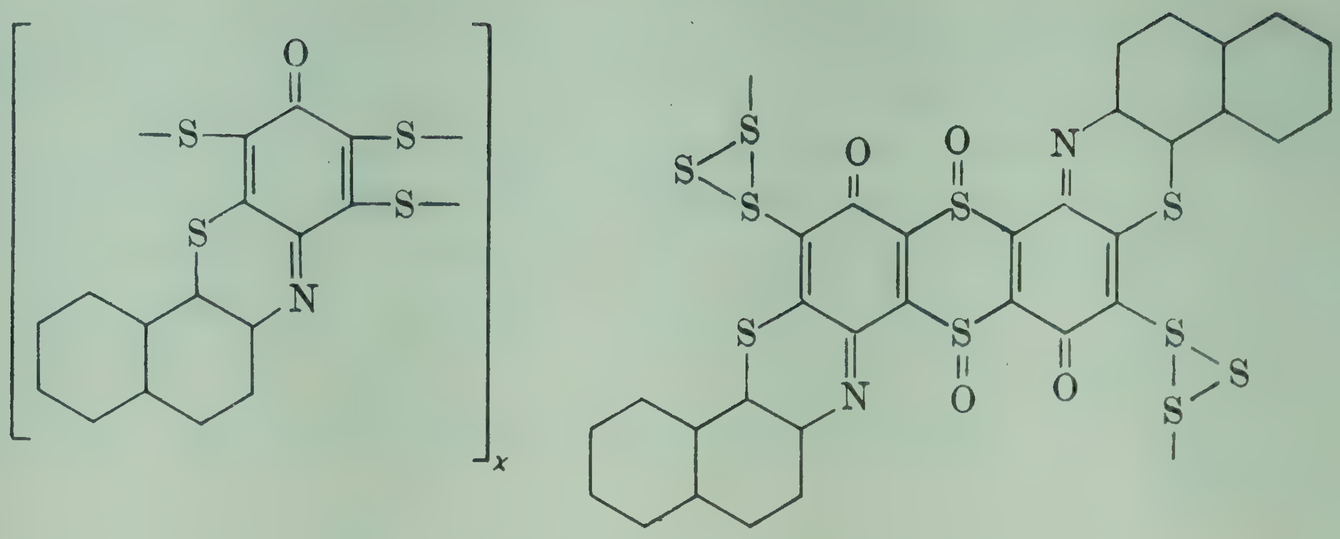


(XXVI)

dye from *p*-hydroxydiphenylamine and (XXV) and (XXVI) for two green dyes from 4-amino-4′-hydroxydiphenylamine.

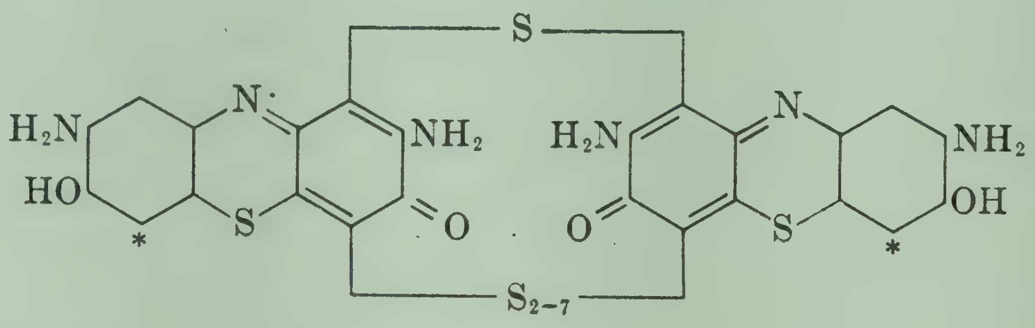
Both the following structures have been suggested by Fierz-David for Indocarbon CL.[92a]

[92a] Fierz-David and Merian, Abriss der Chemischen Technologie der Textilfasern, Verlag Birkhäuser, Basel, 1948, p. 146. See also Fieser and Fieser, Organic Chemistry, 2nd ed., Heath, New York, 1950, p. 930.



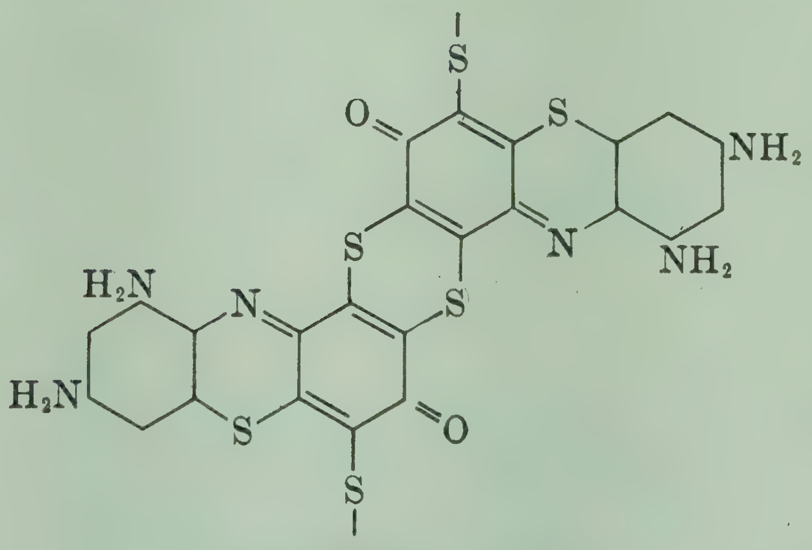
Indocarbon CL

Hiyama assigns the following structure to Sulfur Black T; when the sulfurizing temperature is above 110° sulfur also enters the molecule in the starred positions.[92b]



Sulphur Black T

These structures for various sulfur dyes, including the indicated structure[86] for Immedial Black V, require to be examined further. The available chemical evidence, based on conflicting experimental results, must be



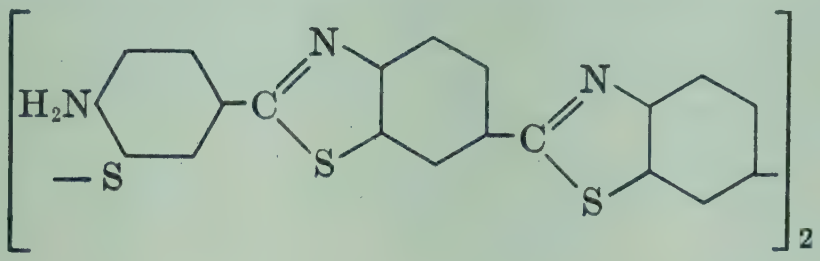
Immedial Black V extra

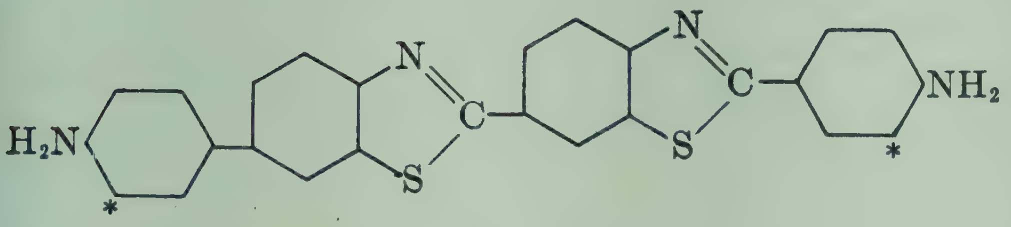
supplemented by X-ray spectrography and other physical investigations. Further attempts to purify sulfur dyes have to be made in the first instance.

[92b] Hiyama, *J. Chem. Soc. Japan Ind. Chem. sect.* **51,** 97 (1948).

Zerweck, Ritter, and Schubert[86] have suggested that Immedial Yellow GG, which is prepared by thionating a mixture of benzidine and dehydrothiotoluidine, consists of four dyes. Three of the dyes are (XXVII) and its derivatives in which one or both the starred hydrogens are replaced by sulfur; and the fourth is (XXVIII). The degradative evidence was based on the conversion of the dyes to the corresponding thioglycolic acids by reduction and condensation with chloroacetic acid; and the proposed structures were confirmed by synthesis. Similar analysis of Immedial Orange indicated that it consists of six to eight molecules of sulfur-substituted *m*-toluylenediamine joined by thiazole rings. The aromatic nucleus may be simultaneously chlorinated.

(XXVIII)

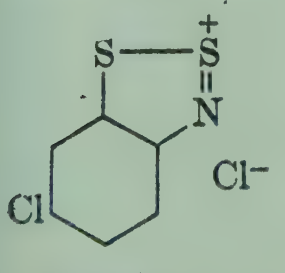




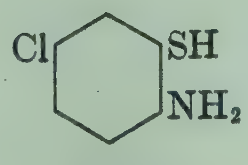
(XXVII)

Stepwise synthesis of sulfur dyes. In order to avoid the ambiguity in the constitution of a sulfur dye which is inherent when it is prepared by a thionation process of heating an intermediate with sulfur or sodium polysulfide, various methods have been developed for the synthesis of sulfur dyes in well-defined stages. Comparison with the sulfur dyes obtained by the usual thionation processes would then give valuable confirmatory evidence of the constitution of the latter. Among these synthetical procedures, the most important is the Herz method, which is also utilized technically in the production of thioindigoid dyes.

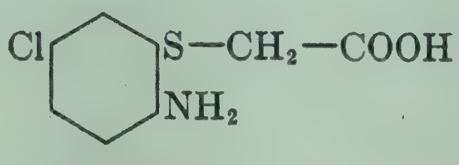
Herz patented the new aromatic substances obtained by the action of sulfur monochloride (S_2Cl_2) on primary arylamines and their substitution products, containing at least one unsubstituted position *ortho* to the amino group.[93] He suggested that the —S—SCl group enters this



(XXIX)



(XXX)



(XXXI)

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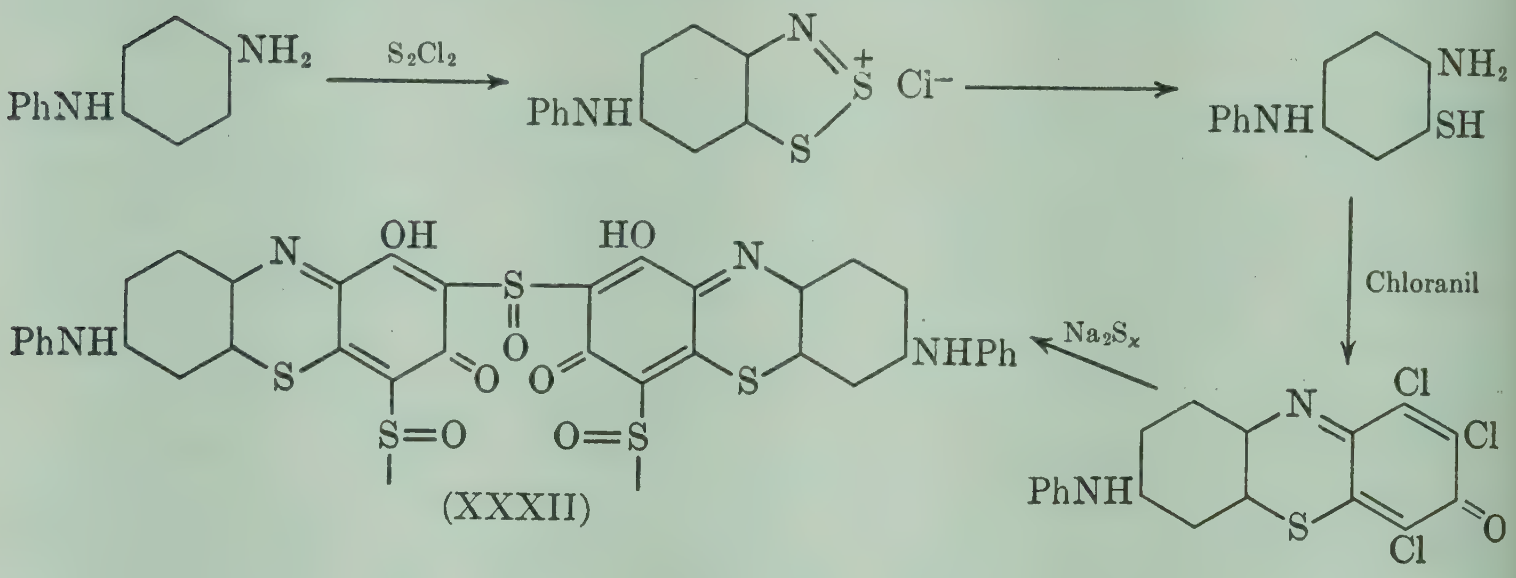
[93] Herz and Grasselli Dyestuff Co., USP 1,699,432 and others; König, *Ber.* **61,** 2065 (1928); see also Blomquist and Diuguid, *J. Org. Chem.* **12,** 718 (1947).

o-position and the product is benzo-1,3-thiaza-2-thionium chloride (XXIX). The compound (XXIX) had the following properties: (1) with water chlorine is replaced by hydroxyl; and (2) with alkalis, the heterocyclic ring opens, and the products (XXX) condense with an alkaline solution of chloroacetic acid to form the *o*-aminoarylthioglycolic acids (XXXI). The value of this reaction in relation to the chemistry of sulfur dyes was indicated by Weiss,[94] and Weinberg[95] used it for the synthesis of sulfur dyes. In the hands of Fierz-David[70] the Herz synthesis has materially increased our knowledge of the constitution of sulfur dyes. A scheme for the synthesis of an analog (XXXII) of Pyrogene Indigo is outlined in Chart 3. For the synthesis of dyes similar to the commercial dyes obtained through polysulfide fusion (e.g. Hydron Blue R), Fierz-David has employed such schemes, but complete identity with the commercial dyes could not be proved. Bernasconi has formulated the synthetic analog of Pyrogene Indigo as the hydroxylated compound (XXXII) containing one hydroxyl group per dibenzothiazine unit; Shibata and Nishi[96] confirm this phenolic structure for (XXXII) and a series of similar dyes on the basis of elementary analysis. Fierz-David,[70] however, has sometimes assumed the complete identity of his synthetic dyes with the commercial prototypes prepared by one-step sulfurization, although the analytical figures did not agree; on other occasions he has merely marked certain positions in his formulas with asterisks without indicating their significance. For one dye, he has formulated a carbon-carbon linkage between pairs of dibenzothiazine units.

CHART 3
SYNTHESIS OF AN ANALOG OF PYROGENE INDIGO



(XXXII)

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[94] *Z. ges. Textil Ind.* **32,** 588 (1929).

[95] *Ber.* **63A,** 117 (1930).

[96] *J. Soc. Chem. Ind. Japan* **38,** Suppl. 41 (1935).

CHAPTER XXXVI

SULFURIZED VAT DYES

Thionation of carbazole-indophenol with alcoholic sodium polysulfide gives a valuable blue dye, Hydron Blue (Haas, 1908; Herz, 1909; CI 969).[1] This discovery was a notable development in the production of dyes by thionation, since it was a new type of sulfur-containing dye which could be applied by vat dyeing processes and had greater fastness, especially to chlorine, than the normal range of sulfur colors. The attractive reddish blue shades on cotton had advantages over indigo, and Hydron Blue soon became one of the bulk products of the dyestuff industry. An interesting and commercially significant feature of Hydron Blue is the use of carbazole as a starting material; an outlet for a coal-tar product which had little use at the time was thus provided, although the present position is different. The large demand for Hydron Blue and for other carbazole derivatives (e.g., tetranitrocarbazole; carbazole plastics) has led to a search for synthetical methods for the preparation of carbazole.

During the same period (1908–1912) in which Hydron Blue and its analogs were developed, it was found by Mayer[2] that the thionation of anthraquinone derivatives gave a new class of sulfur-containing vat dyes. In the present range of Cibanone, Indanthrene and other vat dye series a few belong to this group.

Sulfurized vat dyes are dyes of complex, but more definite constitution than the sulfide dyes, and the probable structures of a few have been elucidated. They occupy an intermediate position between other vat dyes and the sulfide dyes; they are distinguished from the former by their inferior fastness properties and the fact that addition of sodium sulfide is occasionally an advantage in preparing the vats with alkali-hydrosulfite, and from the latter by their greater fastness, insolubility or sparing solubility in sodium sulfide, and by their being dyed from an alkaline hydrosulfite vat. Three types may be distinguished: (a) sulfurized indophenol derivatives, (b) sulfurized anthracene derivatives, and (c) sulfurized diarylaminobenzoquinone derivatives.

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[1] Cassella, DRP 218,371; 221,215; 222,640; 238,857.

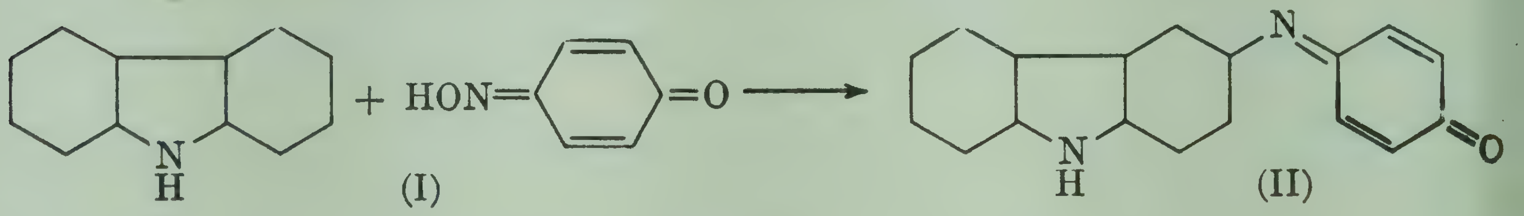
[2] Ciba-DRP, 209,231; 209,233; 211,967; 213,506.

SULFURIZED INDOPHENOLS

When indophenols are used for making sulfide dyes, they are heated with a polysulfide with the approximate composition Na_2S_4. If the proportion of sulfur is increased to Na_2S_{5-8}, the products are insoluble in sodium sulfide and can only be solubilized by vatting with alkaline hydrosulfite. Thus, when the leucoindophenol, 4-dimethylamino-4′-hydroxydiphenylamine, is heated with sodium polysulfide approximating to about the tetrasulfide, the product is Immedial Pure Blue; but when the same intermediate is heated with a higher proportion of sulfur, a vat dye is obtained. The corresponding thiazines can also be employed.[3]

Hydron Blue.[4] The outstandingly important sulfurized vat dyes are the Hydron Blues. The pre-war IG production was over 700 tons annually, the plant capacity being 1000 tons; and the United States production is about 1500 tons (Hydron Blue RG and GA; Sulfanthrene Blue GR and RNN; So-Dye-Vat Blue RD).

There are three stages in the preparation of Hydron Blue R: (a) phenol → *p*-nitrosophenol (I); (b) condensation of (I) with carbazole to form the indophenol (II); and (c) thionation of (II). For the nitrosation of phenol, a solution of sodium phenate and sodium nitrite is added to dilute sulfuric acid at 0°. Carbazole and *p*-nitrosophenol are condensed in concentrated sulfuric acid solution in a lead-lined iron kettle provided both with cooling coils and a cooling jacket. The critical factor is the temperature,which is best maintained at or below −20°. Adequate refrigeration has therefore to be provided in a Hydron Blue plant. The refrigerating plant for Hydron Blue at IG Mainkur supplies calcium chloride solution at −45°. A solution of carbazole (98% pure; 800 kg.) and "anthracene residues" (8) in 95% sulfuric acid (9700), precooled to −28°, is blown into a solution of (I) (670 kg. of aqueous paste = 592 of 100%; 2.5% in excess) in sulfuric acid (4300), cooled to −27°. The addition takes 2 to 3 hours. The indophenol condensation is practically instantaneous, and can be carried out as a continuous process in suitably designed plant.[5] In view of their tendency to



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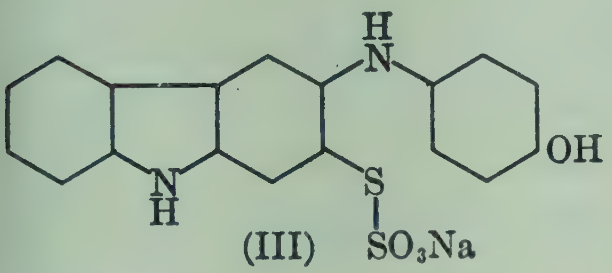
[3] BASF, DRP 153,361.

[4] For a complete account of the IG processes for Hydron Blue, see *BIOS* **983**; *FIAT* **1313** II and III.

[5] Miles, USP 1,516,450.

deteriorate during storage, both (I) and (II) are best used as soon as possible after preparation; dry *p*-nitrosophenol is inflammable on keeping. From the strong sulfuric acid solution, the indophenol is isolated by addition to crushed ice, or as the leuco derivative by addition to caustic soda solution and sodium sulfide or to iron powder and water. The IG process is to divide the batch into three parts, and run each into water (15000), ice (5625) and pin dust (177) at 20–25°; reduction to the leucoindophenol is complete after about 6 hours' agitation. The product is filter-pressed (wooden press with nitrated cotton or polyvinyl cloth), washed completely free from acid and iron, and dried; yield 92.4%. Drying is conveniently carried out on a drum dryer, and the dry leucoindophenol is stable for several months. The indophenol (II) can be estimated gravimetrically by interaction with sodium thiosulfate, which gives the leucoindophenol thiosulfate (III); the latter is then oxidized with ferric chloride to the thiazone (IV) which is weighed.[6] Carbazole-indophenol of the appropriate quality for thionation is reddish blue in color and soluble in acetone, but the most reliable test is a small scale thionation. IG chemists had worked out an improved process for making Hydron Blue, in which the solution of carbazole-indophenol in sulfuric acid is drowned in ice and treated with sodium thiosulfate (1 mole); the thiosulfonic acid thus obtained was readily filterable when the reaction mass was heated with steam and it could be thionated in aqueous solution.[7]



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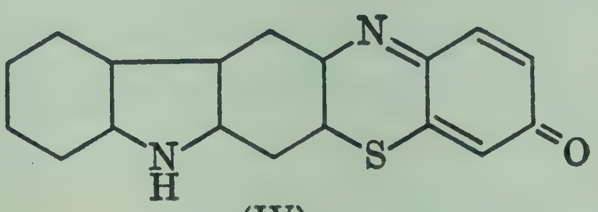

(IV)

Thionation is carried out by means of sodium hexasulfide in butanol; other solvents such as cellosolve can be used. Butanol (95% strength; 5600 kg.), sodium sulfide (60%; 1710) and ground sulfur (2160) are digested at 70° for 30 minutes to form the polysulfide. After cooling to 30°, the indophenol (1800 calculated as 100%) is added. After refluxing for 24 hours, more butanol (1500 l.) and sodium nitrite (90) are added, and the batch held under reflux for a further 2 hours, ammonia being evolved. The solvent is then recovered by steam distillation, for which the batch is divided into six parts. Each is pumped into brine (600 l.) and water (1200), and distilled with steam until a salted-out sample of the distillate shows no more butanol. The final volume is about 3200 l. Free sulfur (as well as any sulfide dye) are now removed by heating with sodium sulfide solution at about 65° for about two hours. Two of the distillation batches are combined and 160 kg. of sodium sulfide crystals are used. The undissolved residue is filter-pressed, and washed with salt water until free from sulfide. The press-cakes from the six parts of the original batch are now taken together, slurried with water (12000 l.), acidified with hydrochloric acid (600–800 kg.), and heated at 50–55° for 30 minutes. The dyestuff is then filter-pressed, washed and dried in a spray dryer. This product is Hydron Blue R, and a redder shade (Hydron Blue RR) is produced by omitting the acid wash. By introducing a process of air oxidation of the dye in suspension in aqueous sodium carbonate at 30° for a few hours, between the desulfurization and acid treatments, Hydron Blue RC is produced.[8]

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[6] Kulikov, *Trans. Leningrad. Chem. Tech. Inst.* **1,** 149 (1934); RP 45,022–3; see also Dornow, *Ber.* **72B,** 568 (1939).

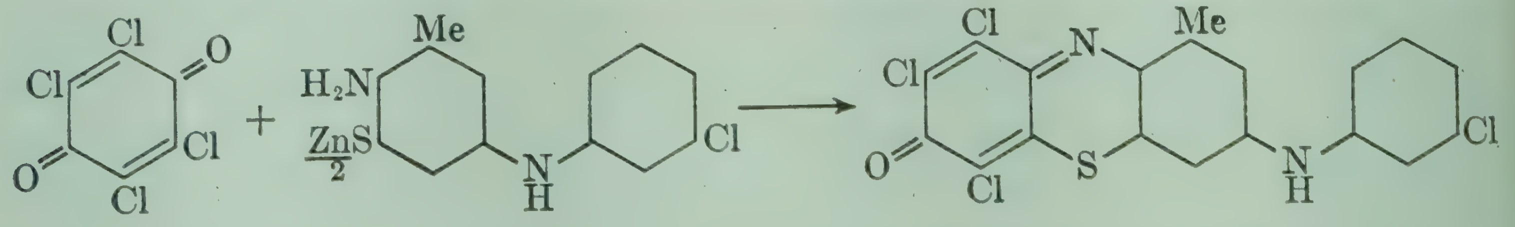
[7] *FIAT* **1313** III.

Carrying out the same thionation with the addition of more sodium nitrite (seven-tenths of the indophenol), Hydron Blue RB is obtained.

Hydron Blue 3R powder highly conc. is prepared by the thionation of a mixture of carbazole-indophenol (1425 kg.), the indophenol ("Immedial Violet Base B"; 150) from *o*-toluidine and (I), 4,4′-dihydroxydiphenylamine ("Immedial New Blue Base G"; 75), and phenol (60) in butanol (5600) by means of caustic soda (1335) and sulfur (2420); further treatments are as for Hydron Blue RC.

Hydron Blue G (CI 971), a greener brand of Hydron Blue, is prepared by thionating the indophenol from N-ethylcarbazole, admixed with a tenth of its weight of dihydroxydiphenylamine. Hydron Blue GT is the product of thionation of the same indophenol and 15% of phenol with sulfur and caustic soda in butanol solution. The Hydron Blues are mixed and ground for standardization in an atmosphere of nitrogen.[4]

A sulfurized vat dye of the indophenol type, which is however not prepared from an indophenol, is Hydron Printing Blue 3R (Indanthrene Printing Blue 3R) (IG).[9] The method is to condense chloranil with the zinc salt of 3-chloro-4′-amino-3′-mercapto-5′-methyldiphenylamine (V) in alcohol.



(V)

Indanthrene Printing Blue 3R

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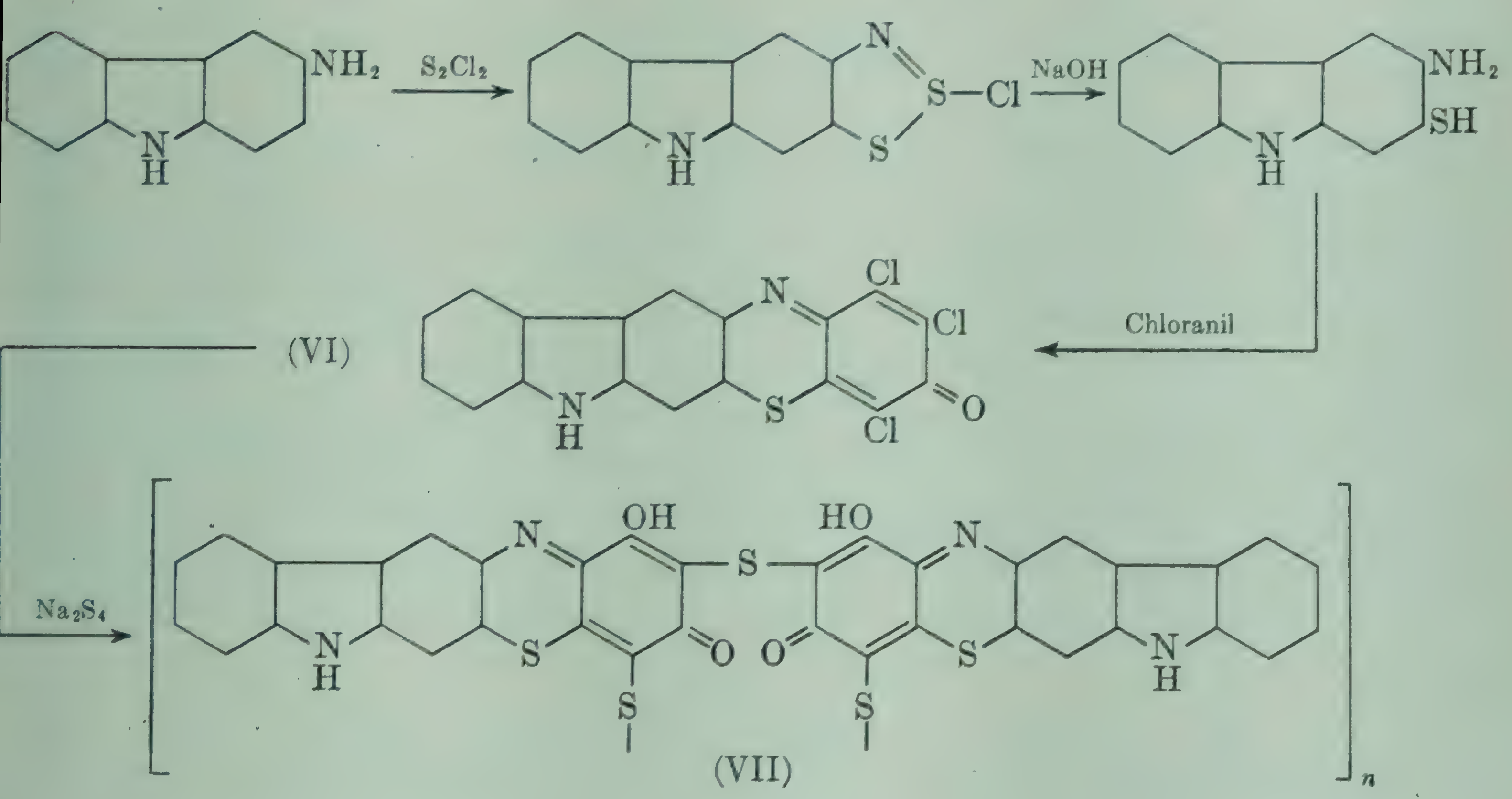
[8] According to *BIOS* **983,** however, the C in RC merely indicates that the color is made in spirit C (butanol), and the R and RC brands are practically identical.

BIOS **987.**

Green dyes of the Hydron Blue type are produced by using naphthocarbazole and dinaphthocarbazole in place of carbazole, and adding copper salts in the sulfide fusion.[10]

The constitution of Hydron Blue. The elementary analysis of Hydron Blue, purified by a method of exhaustive extraction (see Chapter XXXV), corresponds to the formula $C_{31}H_{16}N_4O_5S_5$.[11, 12] The dye molecule is probably a polymer of this unit. When the dye was solubilized by heating with monohydrate and chlorosulfonic acid at 90–95° for 20 hours, and the aqueous solution titrated against titanous chloride, Fierz-David and Bernasconi found that the titer indicated the presence of two thiazine rings per unit of the dye molecule. Attempts to reduce the dye to a mercaptan by means of glucose and alkali and prepare a thioglycolic acid by condensation with chloroacetic acid were unsuccessful, since the product was very unstable. The constitution of Hydron Blue was then approached from the synthetic angle.[11, 13] 3-Amino-2-mercaptocarbazole was made from 3-aminocarbazole by the Herz method, and condensed with chloranil to form the thiazone (VI). Treatment of (VI) with sodium tetrasulfide gave a dye which analysed correctly for the structure (VII) and resembled Hydron Blue in its dyeing properties. When the synthesis was repeated, using trichlorotoluquinone and dichloro-*p*-xyloquinone respectively in place of chloranil, the first product



(VI)

(VII)

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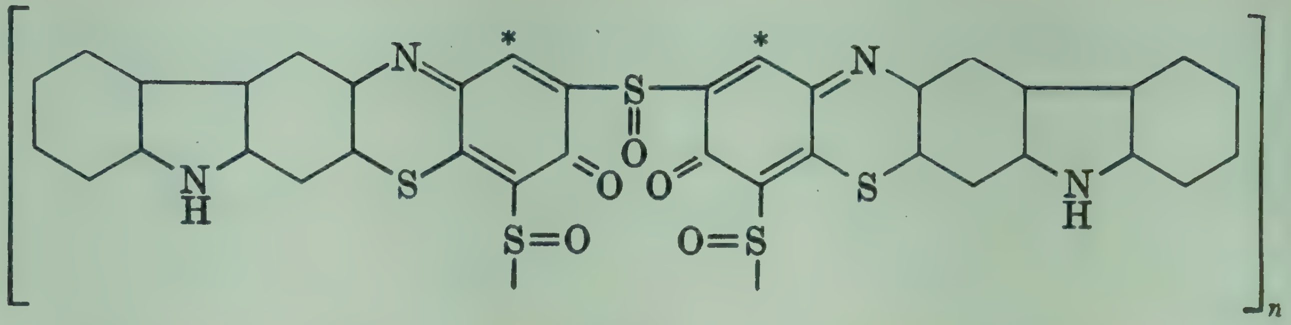
[10] IG, BP 381,265.

[11] Fierz-David *et al.*, *J. Soc. Dyers Colourists* **51,** 50 (1935).

[12] Hiyama, *Kwagaku to Kōgkō (Science and Ind.)* **16,** 230 (1941).

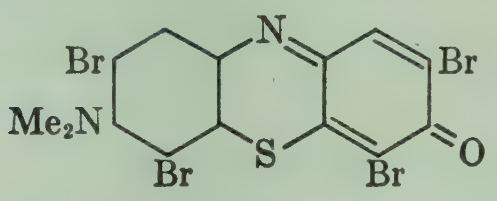
[13] Shibata and Nishi, *J. Soc. Chem. Ind. Japan* **38** Suppl. Bind. 41 (1935).

(VIII)



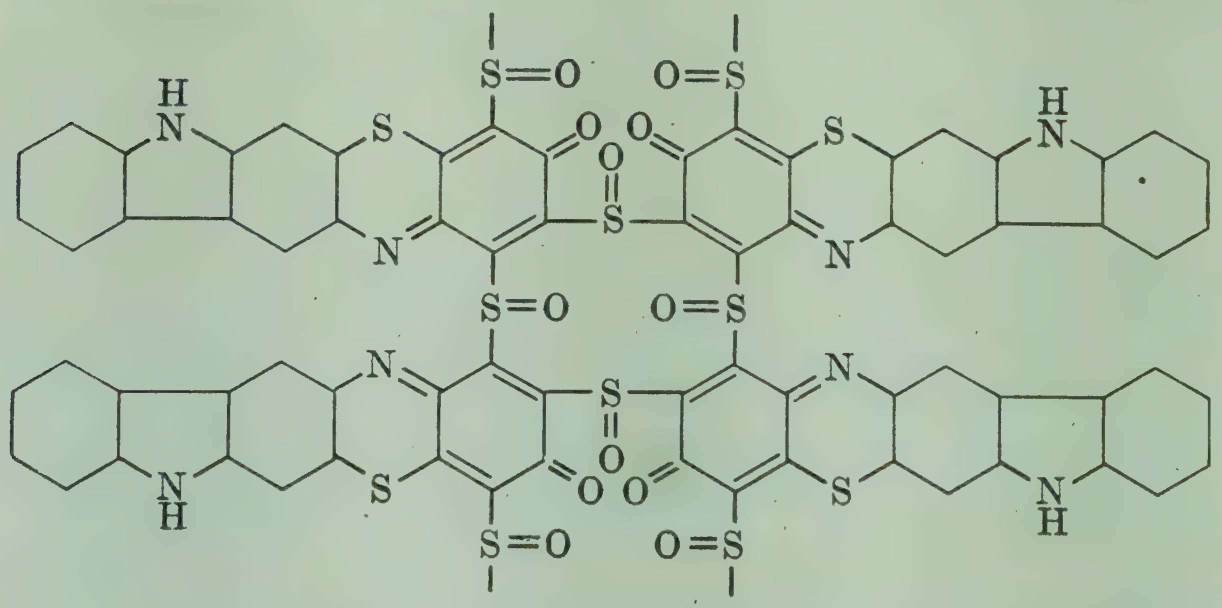
had poor tinctorial power, and the second did not behave as a sulfide or vat dye at all. On the basis of these results the structure (VIII) was assigned to Hydron Blue; similar structures were suggested for Immedial Pure Blue and Pyrogene Indigo on analogous grounds.

The constitution (VIII) for Hydron Blue can be valid only if n stands for two, or if polymerization has taken place by a carbon-carbon linkage at the starred position. The latter possibility is unlikely on the assumption that Hydron Blue and Immedial Pure Blue are similarly constituted,



(IX)

since Gnehm and Kaufler[14] brominated Immedial Pure Blue and obtained (IX), the constitution of which is shown by its being the product of the bromination of Methylene Violet. The absence of carbon-carbon linkages between the indophenol units has been confirmed by the fact that Raney nickel reduction of both Hydron Blue and carbazole-indophenol gives the same product.[15] The thionation products of the indophenols obtained by the condensation of carbazole with 5-nitroso-*o*-cresol and 6-nitroso-*m*-cresol respectively have dyeing properties very different from and inferior to those of Hydron Blue, the shades being weak gray



(X)

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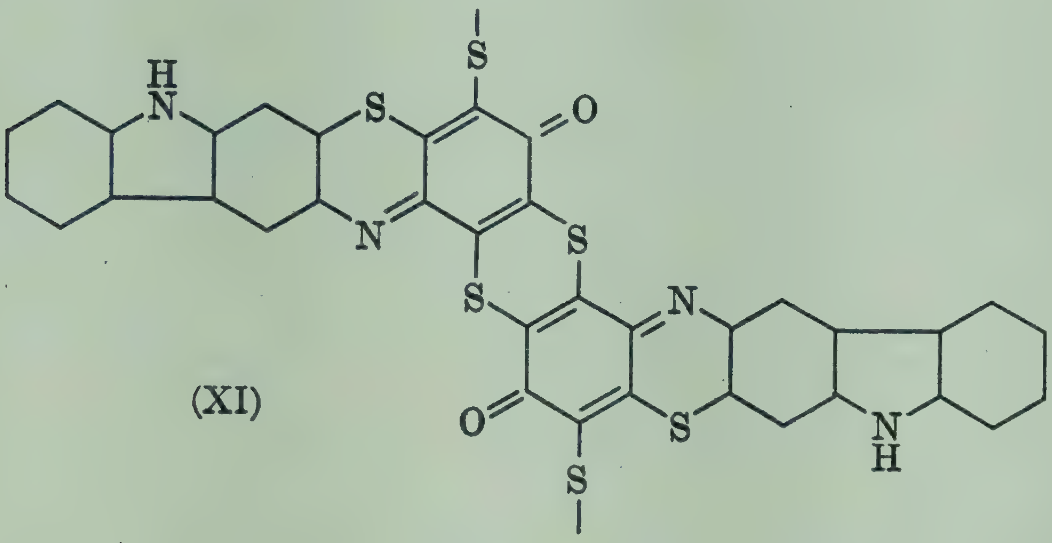
[14] *Ber.* **37**, 2618 (1904).

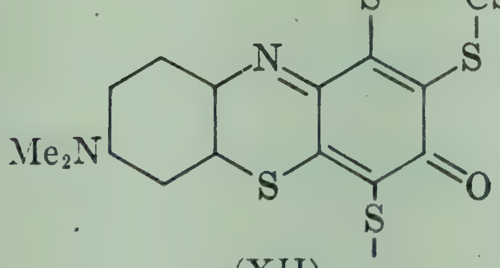
[15] Shah, Tilak, and Venkataraman, *Proc. Indian Acad. Sci.* **28**, 111 (1948).

and grayish blue. This indicates that all the three vacant positions in the quinone residue of the thiazone (IV) are necessary for the formation of Hydron Blue by attachment of sulfur. The constitution (X) for Hydron Blue accounts for the available data better than (VIII).

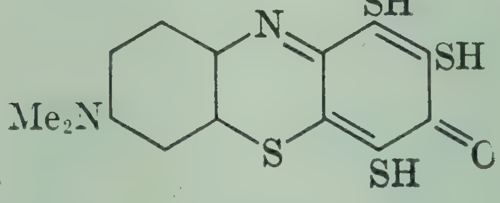
According to Zerweck, Ritter and Schubert Hydron Blue has the structure (XI) containing thianthrene rings, and similar structures have been proposed for other sulfurized indophenols.[15a] Their suggestion is based on the following considerations, but experimental details and analytical data have not been provided. Sulfur must enter the 1-, 2-, and 4-positions in a thiazone such as (VI), since the products did not have the dyeing properties of the Immedial Pure Blue or Hydron Blue type of dye if one of the three positions was blocked by a methyl, phenyl or other group irreplaceable by sulfur; this has also been shown by other workers.[15] Trichloro-Methylene Violet reacted with trithiocarbonate to form (XII), and subsequent reduction and mild treatment with sodium sulfide gave (XIII). The trimethyl ether of (XIII) was crystallized and analysed. Oxidation of (XIII) yielded a poly-disulfide, which dissolved in aqueous sodium sulfide more readily than Immedial Pure Blue and had inferior dyeing properties (contrast Meyenberg and Levy's work mentioned earlier). However, Zerweck *et al.* do not exclude disulfide linkages from



(XI)



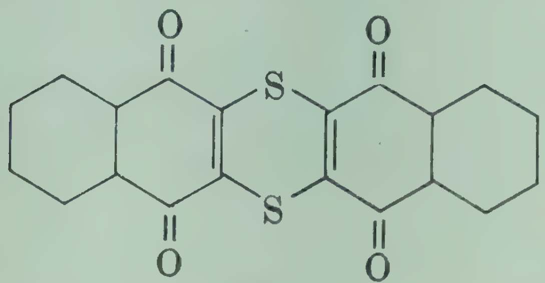
(XII)

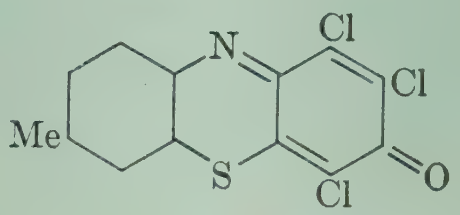


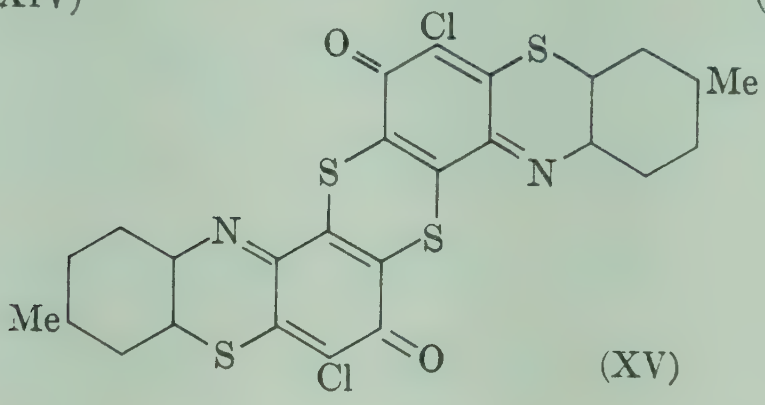
(XIII)

[15a] *Angew. Chem.* **60A,** 141 (1948).

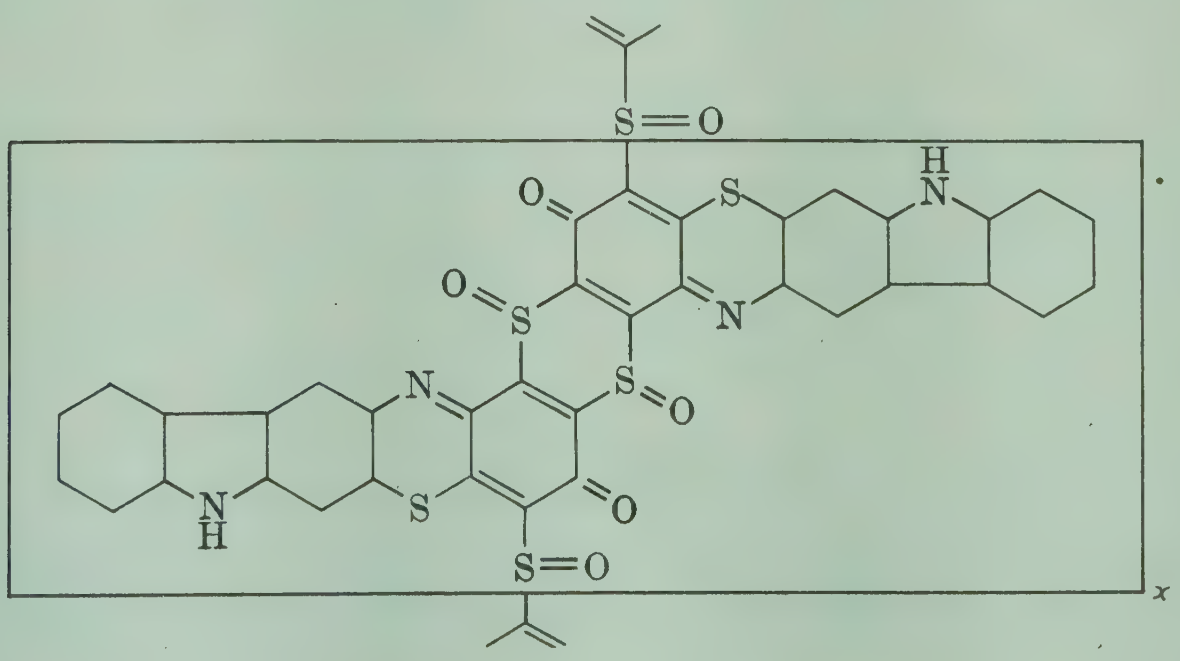
the structures for Immedial Pure Blue and Hydron Blue, although the leuco compounds condense with chloroacetic acid to di- and not tetra-acetic acids. They believe that positive evidence for thianthrene rings is provided by the formation of the thianthrene (XIV) from 2,3-dichloro-1,4-naphthoquinone,[15b] and a crystalline substance regarded as (XV) and


(XIV)


(XVI)


(XV)

obtained in 45% yield from 1,2,4-trichloro-7-methylphenothiazone (XVI). The evidence for (XV) was that analysis indicated two chlorine atoms. The absorption of oxygen by the thianthrene rings to form bis-sulfoxides and the addition of sulfur at the disulfide bridges to form polysulfides are considered by Zerweck *et al.* to be phenomena which account for changes in the properties of sulfur dyes during storage, drying, vatting and other processes. If Hydron Blue can be synthesized from an intermediate such as the unknown 1,5-dihydroxythianthrene, the structure (XVII) would merit consideration.


(XVII)

[15b] Brass and Köhler, *Ber.* **55**, 2543 (1923).

Dyeing and fastness properties of Hydron Blue. Hydron Blue R and RR are useful for the production of navy and dark blue shades on cotton, especially in piece dyeing, and were marketed as competitors to indigo. They may be dissolved (a) by means of sodium sulfide, hydrosulfite and caustic soda at about 70°, the hydrosulfite being added towards the end; or (b) by hydrosulfite and caustic soda at about 60° (like the IN process for anthraquinonoid vat dyes, but using less caustic soda). These alkaline vats are yellow in color. In the first and cheaper method, dyeing may be carried out near the boil or at about 60°. The hydrosulfite vat gives brighter shades. The Hydron Blues have good leveling properties. After dyeing, the material is oxidized by air; the shades can be brightened by aftertreatment with sodium perborate or hydrogen peroxide, but the fastness to washing is slightly reduced. In their fastness properties the Hydron Blues are superior to the Sulfur Blues; they are inferior to the anthraquinone vat blues in light fastness, but better in chlorine fastness than many of the anthraquinone vat blues. The fastness figures are light 6, washing 4–5 and chlorine 3.

Sulfurized Anthracene or Anthraquinone Derivatives

Unlike the indophenol thionations which are carried out with sodium polysulfide in an alcoholic solvent, the sulfurization of anthracene derivatives is a baking process with elementary sulfur. When anthracene is heated with four times its weight of sulfur at 270–300°, Hydron Olive G (C; CI 1168) is formed. Indanthrene Olive 3G (formerly Hydron Olive GN) has been stated (ST Erg. II) to be the product of the thionation of anthracene by means of sulfur monochloride; but the dye marketed later under this name is not a sulfurized vat dye (see Chapter XXXI). Weinberg[16] has found that the action of sulfur monochloride on anthracene results in the introduction of six atoms of sulfur and four of chlorine per mole of anthracene. Two chlorine atoms are exchangeable by aniline groups, and all the four by mercapto groups; the tetramercapto derivative can be methylated to the tetramethyl thioether. According to Kalischer *et al.*,[17] 1,8- and 9,10-dichloro-, 2,9,10-trichloro-, and 1,3,9,10-tetrachloroanthracene give the same dye. Modified shades are obtained by the addition of metallic oxides. Indanthrene Dark Blue GBE has been stated to have been prepared by melting anthracene with sulfur, sulfur chloride and a small amount of mercuric chloride;[18] but according to Fierz-David[19] it is prepared by the alkylation of Hydron Olive GN.

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[16] *Ber.* **63,** 129 (1930).

[17] USP 1,758,365.

[18] *Bibl. Sci. and Ind. Repts.* **7,** 761 (1948).

[19] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935.

Other polynuclear hydrocarbons (acenaphthene, phenanthrene, pyrene, chrysene), their hydroxy, amino, and arylamino derivatives can be sulfurized to form brown, orange, olive, greenish-blue, dark green, and black dyes with good fastness on cotton.[20]

Cibanone Yellow R and Orange R. By fusing 2-chloromethylanthraquinone or its chloro derivatives with sulfur and treating the product with sodium hypochlorite a bright orange-yellow dye, Cibanone Yellow R (Mayer and Schaarschmidt, 1908; CI 1170) is obtained. Cibanone Orange R (CI 1169) is made similarly by thionation at a higher temperature.[2, 11, 21] Cibanone Yellow R and Orange R dye bright, attractive shades with excellent fastness to chlorine (5); the light fastness grade is only 4 for Yellow R, but 6–7 for Orange R. Both these dyes have however been withdrawn from the commercial range of Cibanone colors because of their tendering action on cellulose when the dyed material is exposed to light. This catalytic activity of Cibanone Yellow R and Orange R is indeed so marked that they have been the dyes of choice for investigating the accelerated oxidation of cellulose by the action of light and of oxidizing agents (see Chapter XL). When cotton dyed with a mixture of Cibanone Yellow R (or Orange R) and an innocuous dye, such as Caledon Jade Green, possessing excellent fastness to light, is exposed to light, the green dye fades rapidly. It is a curious fact that, notwithstanding this unpleasant property of Cibanone Yellow R, similar dyes have been marketed (Calco Yellow 5G; Calcosol Printing Yellow 5G; Sulfanthrene Yellow R; Anthra Yellow GDN). An examination of Cibanone Yellow R and Calco Yellow 5G has shown that the two dyes behave alike in their dyeing properties, color reactions and photochemical activity.[22]

The constitution of Cibanone Yellow R and Orange R has been examined by Fierz-David and Geering.[11] After removal of inorganic salts by means of hot water, the commercial dyes were extracted with alcohol, and from the extract of both the dyes 2-methylanthraquinone was isolated. Elementary analysis of purified Yellow R gave C, 76.1; H, 3.4; S, 8.5% ($C_{30}H_{16}O_4S$ requires C, 76.2; H, 3.4; S, 6.8%). The molecular weight by Rast's method in perylene was 495 ($C_{30}H_{16}O_4S$ requires m.w. 472). Chromic acid oxidation gave anthraquinone-2-carboxylic acid; but the dye was stable to hydrogen peroxide. From these results it was concluded that the dye was probably a bis-anthraquinonethiopyran (diphthaloylthioxanthene; I or II). The condensation of phthalic anhydride and thioxanthene in presence of aluminum chloride, followed by cyclization, gave a product, which was considered to be the linear compound (II) in view of the observation of Scholl and Seer[23] that

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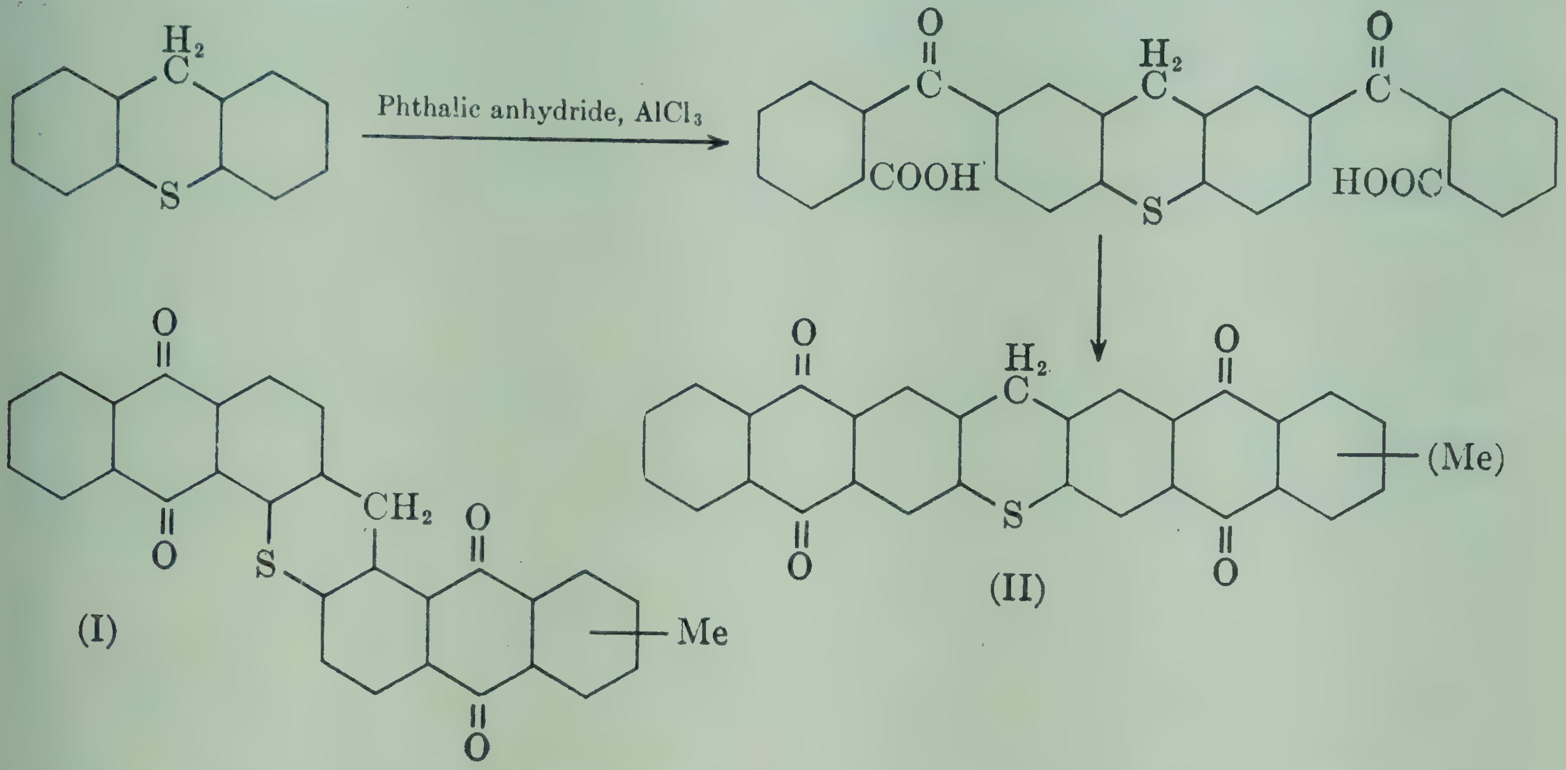
[20] Ciba, BP 431,976; 435,342; USP 2,027,323; IG, DRP 658,073.

[21] According to Thomson (Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. I, Longmans, London, p. 423), Cibanone Black B is prepared by the sulfur fusion of 2-methylanthraquinone at 300–330°; but this is obviously erroneous (*vide infra*).

[22] Chandavarkar and Tilak, unpublished work.



(I)

(II)

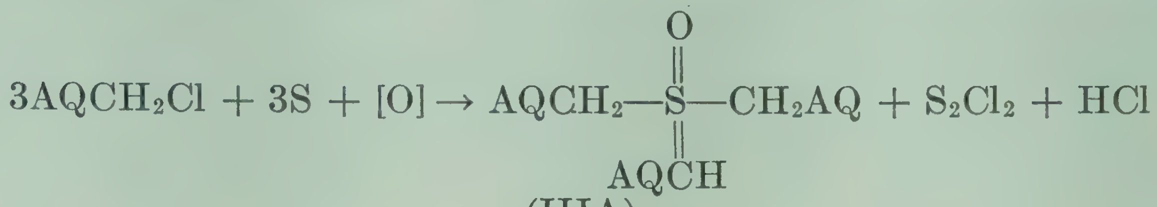
o-diphenylenedisulfide (thianthrene) gave a linear compound (II; S in place of CH_2) by phthalic anhydride condensation and subsequent cyclization. However, Fierz-David and Geering obtained values for carbon and sulfur which were substantially different from the theoretical requirements for (I) and (II). The compound dyed much weaker shades than Cibanone Yellow R, to which the angular structure (I) was then assigned. There are several considerations which render the constitution (I) very improbable; e.g. the difference in the sulfur content between the theoretical and experimental values, and the fact that by oxidative fission anthraquinone-1-carboxylic acid was not isolated in addition to the 2-acid. Shah and Tilak[24] have re-examined the chemistry of Cibanone Yellow R and Orange R, and have found that the purified Yellow R of Fierz-David and Geering is a mixture of several substances. When a solution of the purified Yellow R in acetylene tetrachloride was chromatographed on alumina, three small bands developed on the column, and concentration of the percolate gave yellow needles, m.p. 368–370°, considered to be the essential tinctorial constituent of Cibanone Yellow R from the dyeing and other properties. This would appear to be the first instance of a sulfur dye or sulfurized vat dye being isolated as a crystalline material with a definite melting point. Further concentration of the

[23] Scholl and Seer, *Ber.* **44,** 1233 (1911).

[24] *Proc. Indian Acad. Sci.* **30A,** 1 (1949).

mother liquor gave Anthraflavone. Elementary analysis of pure Cibanone Yellow R gave C, 76.1; H, 3.6; S, 4.4 ($C_{45}H_{26}O_7S$ requires C, 76.1; H, 3.7; S, 4.5%).

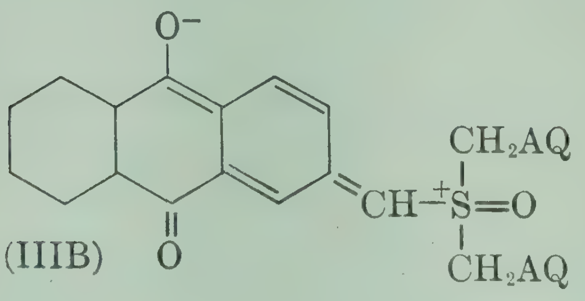
Taking into consideration the method of preparation of Cibanone Yellow R from 2-chloromethylanthraquinone, as well as its properties, it is suggested that the dye has the constitution (III) and is probably formed by the following overall reaction (AQ = β-anthraquinonyl).



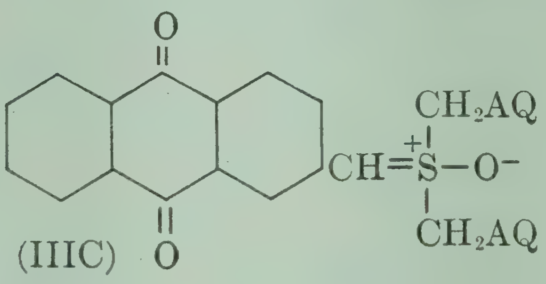
$$3AQCH_2Cl + 3S + [O] \rightarrow AQCH_2-\overset{\overset{O}{\|}}{\underset{\underset{AQCH}{\|}}{S}}-CH_2AQ + S_2Cl_2 + HCl$$

(IIIA)

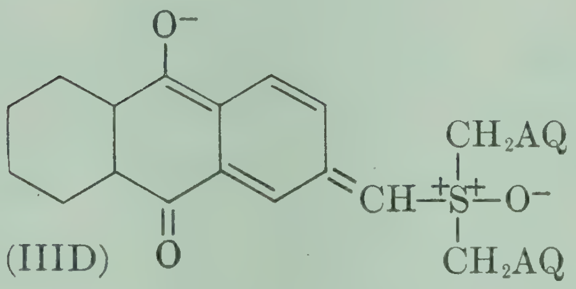
The intense yelow color of the dye and its stability are associated with resonance among structures such as (A), (B) (C), and (D). An alternative structure (IV), derived from Anthraflavone, can be suggested for pure Cibanone Yellow R in view of the following: (1) the nearly quantitative conversion of bis-2-anthraquinonylmethyl sulfide ($AQCH_2SCH_2AQ$) by heating at 250° to Anthraflavone; (2) the occurrence of Anthraflavone in the commercial dye; and (3) the possibility of an addition reaction between Anthraflavone and 2-mercaptomethylanthraquinone ($AQCH_2SH$). A third structure which can be postulated is 2,4,5-tri-β-anthraquinonyl-1,3-oxathiole, and further investigation, including Raney nickel reductions and the synthesis of model sulfur-containing compounds derived from β-methylanthraquinone, is in progress.[22]



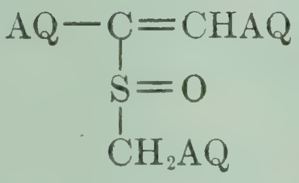
(IIIB)



(IIIC)

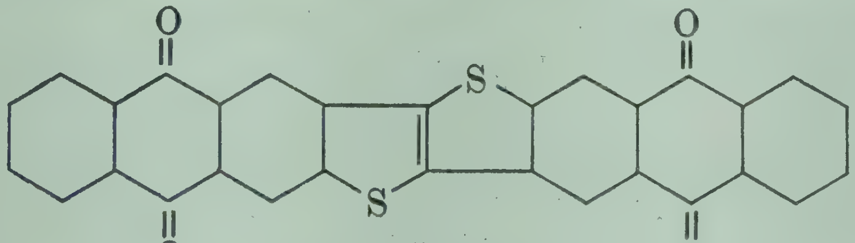


(IIID)

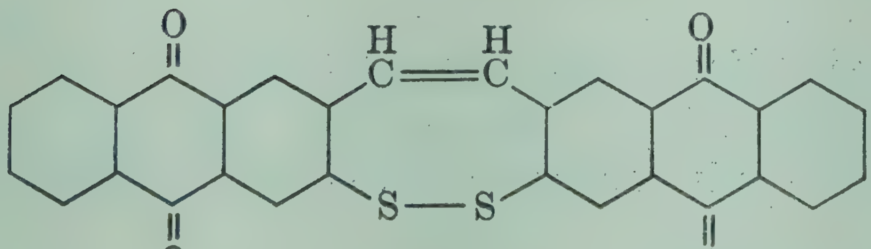


(IV)

Schaarschmidt and Lewyoff crystallized commercial Cibanone Orange R from nitrobenzene and have stated that analysis of the crystalline material (m.p. > 500°) indicates a sulfur content corresponding to one atom of sulfur for one mole of 2-methylanthraquinone in the dye molecule.[25] Reduction and oxidation experiments gave no positive results, and details such as the actual percentage of sulfur are not mentioned. Fierz-David and Geering, who have not referred to Schaarschmidt and Lewyoff, have purified the dye by their usual exhaustive extraction method; the dye itself was somewhat soluble in alcohol, so that the duration of the alcohol extraction had to be curtailed. The analytical values were found to agree best with the formula $(C_{15}H_6O_2S)_x$, and Cibanone Orange R was regarded as being related to Yellow R in the same way as Primuline to dehydrothiotoluidine.[11] From a study of oxidation-reduction potentials, Atherton and Turner[26] have concluded that the Cibanone Orange R molecule contains two anthraquinone groups; catalytic reduction of the dye, reoxidation of the leuco compound, and determination of the hydrogen peroxide formed gave a value of 513 for the molecular weight. Shah and Tilak[24] have found that Cibanone Orange R, purified according to Fierz-David and Geering, contained about 10% of Cibanone Yellow R, isolated by chromatographing a solution in acetylene tetrachloride, so that neither Fierz-David and Geering nor Atherton and Turner were dealing with a homogeneous chemical compound. Cibanone Orange R would appear to contain an Anthraflavone skeleton. Distillation of either Cibanone Orange R or Anthraflavone with zinc dust, zinc chloride and sodium chloride (Clar reduction) gave 2-methylanthracene as one of the products, and oxidation of either dye with nitric acid in acetic acid gave anthraquinone-2-carboxylic acid. Treatment of 2-methylanthraquinone with sulfur at 300° under reduced pressure gave 2,2′-dianthraquinonylethane (dihydroanthraflavone), and at 360° a dye identical in all its properties with Cibanone Orange R. Dihydroanthraflavone itself also gave a similar dye on heating with



(V)



(VA)

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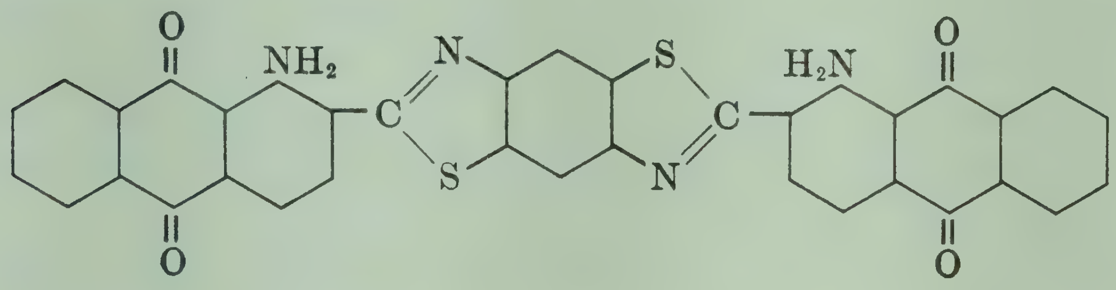
[25] *J. prakt. Chem.* **113,** 48 (1926).

[26] *J. Soc. Dyers Colourists* **62,** 108 (1946).

sulfur at 360°. Thionation did not take place at the 1-position in 2-methylanthraquinone and the 1,1′-positions in dihydroanthraflavone, since thionation of 1-chloro-2-methylanthraquinone did not yield Cibanone Orange R. On the other hand, 3-chloro-2-methylanthraquinone gave a dye closely similar to Cibanone Orange R. The fused dithiopheno (or thiophthene) structure (V) satisfies the available evidence. The structure (VA) is less probable, although it cannot be ruled out at the present stage.[22]

Cibanone Brown B (CI 1171) is prepared from 1-amino-2-methylanthraquinone by sulfur fusion at about 300°; the brown shades from a dark brown hydrosulfite vat have chlorine fastness 3 and light fastness 5. Heating 1-amino-2-methylanthraquinone (110), *p*-phenylenediamine (32) and sulfur (325) at 200–230° for a few hours, the product is Hydron Violet N, which is obsolete and is used only for shading the Hydron Blues.[9]


Hydron Violet N

When 4-methylbenzanthrone is sulfurized in boiling naphthalene, the product is Cibanone Blue 3G[27] (Mayer and Pfannenstiehl, 1908; CI 1173). At a higher temperature (300–330°) and in the absence of a solvent, the action of sulfur on 4-methylbenzanthrone gives Cibanone Black B, 2B or 2G (CI 1172). Although the fastness properties of Cibanone Blue 3G are only moderate like those of other sulfurized vat dyes of this type, it is useful in calico printing. Cibanone Blue 3G is identical with Indanthrene Blue Green FFB (Lüttringhaus, Nawiasky and Ehrhardt, 1927), made by a different method[9, 28] (Chart 1), which yields the dye in a much purer form than the Ciba sulfurization process and also provides proof of the constitution of Cibanone Blue 3G. The interaction of 4-methylbenzanthrone with sodium polysulfide gives Cibanone Green B (Mayer, 1912; CI 1174); this is also obtained by oxidizing Cibanone Blue 3G with manganese dioxide or nitric acid and concentrated sulfuric acid at room temperature.[29] Cibanone Blue 3G and Green B have a light fastness of 6–7, but the fastness to soda-boil and to chlorine are only moderate (3), Green B being slightly superior.

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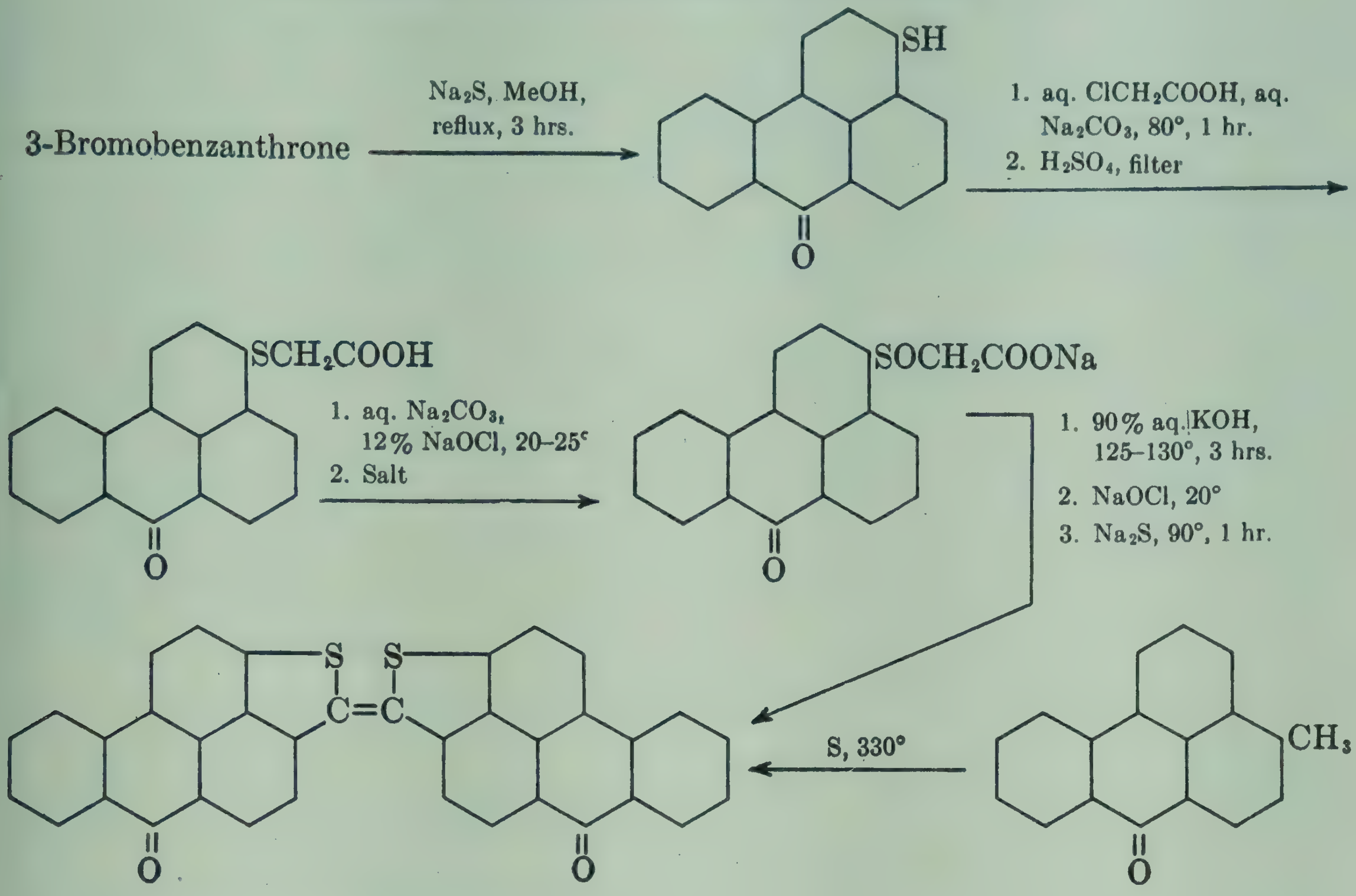
[27] Ciba, DRP 209,351; 243,751.

[28] IG, DRP 483,154.

[29] Böhner and Ciba, DRP 261,557; 265,194.

CHART 1
Preparation of Indanthrene Blue Green FFB


3-Bromobenzanthrone
Na₂S, MeOH, reflux, 3 hrs.
SH
O
1. aq. ClCH₂COOH, aq. Na₂CO₃, 80°, 1 hr.
2. H₂SO₄, filter
SCH₂COOH
O
1. aq. Na₂CO₃, 12% NaOCl, 20–25°
2. Salt
SOCH₂COONa
O
1. 90% aq. KOH, 125–130°, 3 hrs.
2. NaOCl, 20°
3. Na₂S, 90°, 1 hr.
S
S
C=C
O
O
S, 330°
CH₃
O

Indanthrene Blue Green FFB

Both require care in dyeing since their leveling properties are poor. Oxidation of Cibanone Blue 3G in nitrobenzene solution with nitric acid gives Cibanone Olive B[29] (CI 1175). The result of oxidation of Cibanone Blue 3G would appear to be the introduction of hydroxyl groups, probably in the 2,2′-positions of the benzanthrone residues.[30]

By heating 2,6-diaminoanthraquinone, benzotrichloride (excess), sulfur and a little cuprous chloride in a naphthalene melt at about 220° for several hours, Algol Yellow GC (IG) (Isler and Kačer, 1912) is produced.[11, 31, 32] The dye may also be prepared in stages, when a better yield is obtained (Chart 2).[9] The crude dye is dispersed by dissolving in concentrated sulfuric acid and drowning in water, and then oxidized by means of hypochlorite. Algol Yellow GC dyes a pure yellow from a

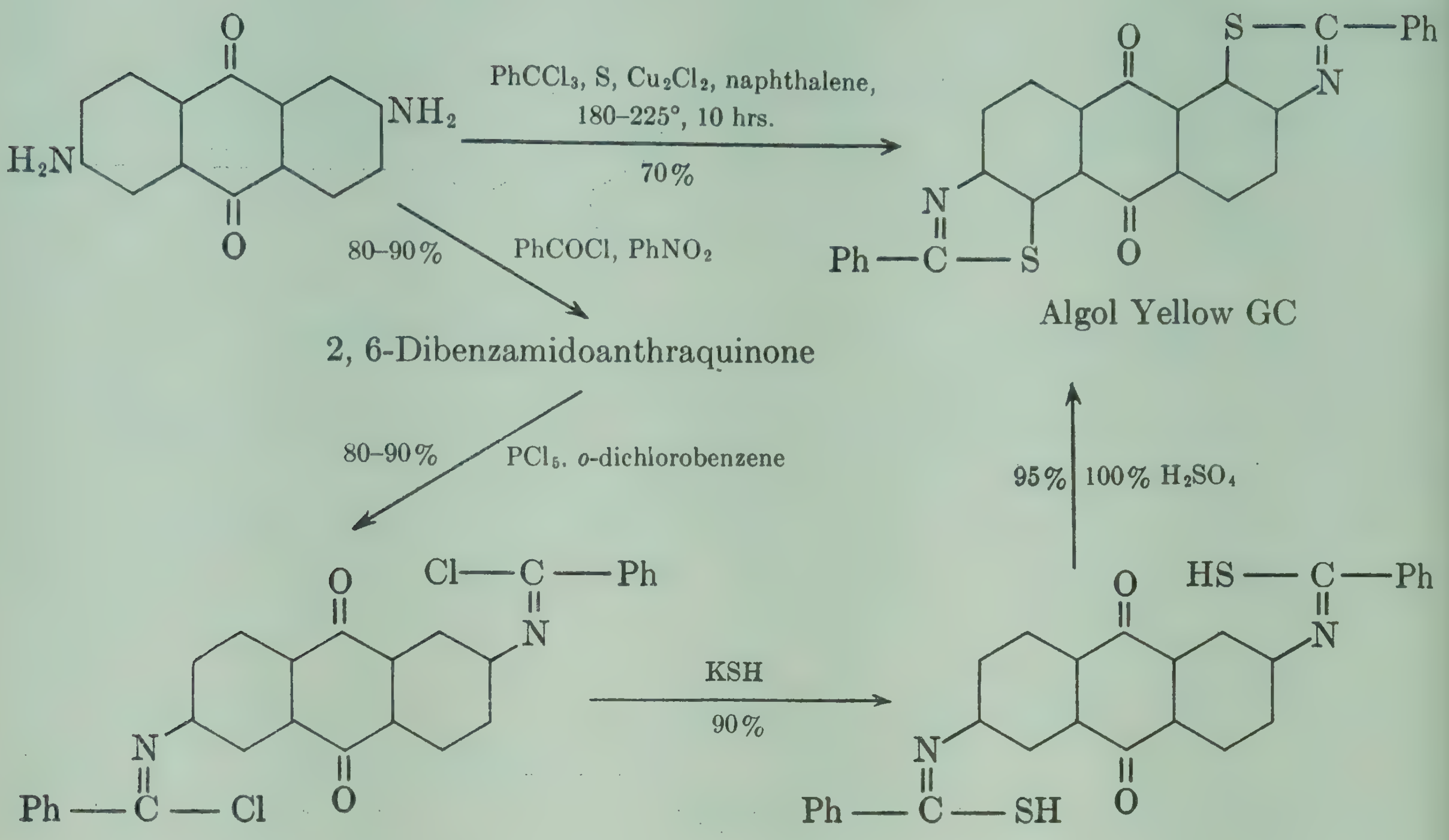
[30] Thomson, Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. I Longmans, London, p. 419.

[31] Unger, Böhner and IG, DRP, 492,447. See also Fleysher and Allied Chemical and Dye Corp., USP 2,473,872; American Cyanamid, USP 2,289,292. Mixtures of 2,6- and 2,7-diaminoanthraquinones are stated to give better yields than 2,6- alone, and the 3,7- or 3,6-dichloro or 1,3,5,7- or 1,3,6,8-tetrachloro derivatives of these diamines can be used; du Pont, USP 2,150,092; 2,164,784.

[32] According to Ref. 19, Algol Yellow GC and Anthra Yellow GC are identical, but the latter dye is stated in CI, p. 372 to be the same as Anthraflavone.

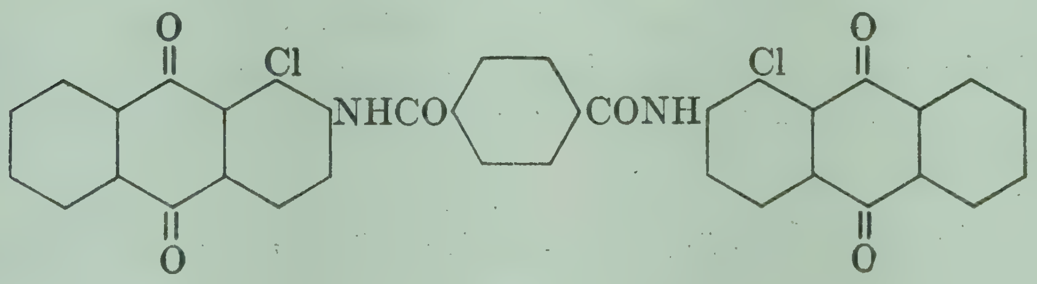
CHART 2

Preparation of Algol Yellow GC

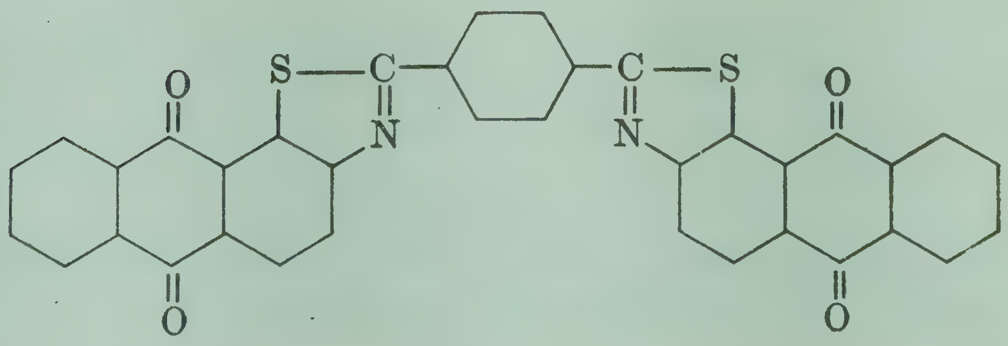

H₂N
NH₂
PhCCl₃, S, Cu₂Cl₂, naphthalene,
180–225°, 10 hrs.
70%
80–90%
PhCOCl, PhNO₂
2, 6-Dibenzamidoanthraquinone
80–90%
PCl₅. o-dichlorobenzene
Algol Yellow GC
95%
100% H₂SO₄
KSH
90%
Ph—C—Cl
Cl—C—Ph
Ph—C—SH
HS—C—Ph
Ph—C—S
S—C—Ph

red-violet vat. The fastness properties are only moderate, the fastness to light being 3–4, but the dye is useful for the bright green shades it gives on admixture with the Caledon Jade Greens. Paradone Yellow GC (LBH) is identical in structure with Algol Yellow GC, but is prepared[30] by heating a mixture of benzaldehyde and 1,5-dichloro-2,6-diaminoanthraquinone with sulfur. A dye, which is somewhat faster than Algol Yellow GC, but is uneconomical to produce, is Algol Yellow GGC, prepared by the sulfurization of the condensation product (VI) of 1-chloro-2-aminoanthraquinone and terephthalic acid.[9]

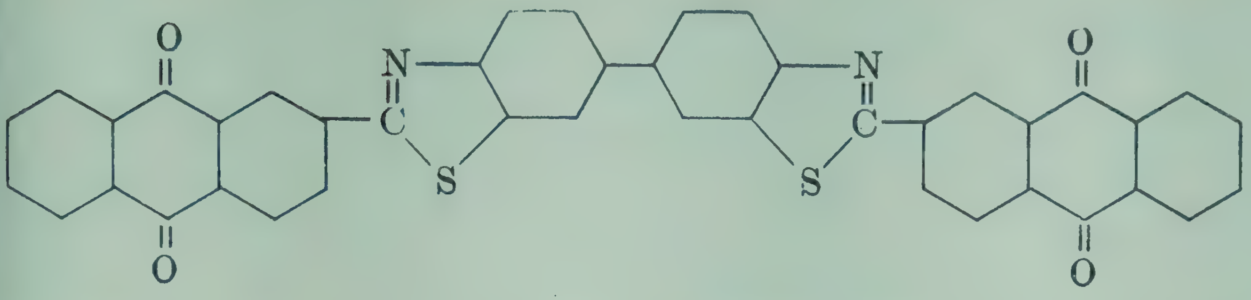
Another type of thiazole derivative is Indanthrene Yellow GF obtained by heating β-methylanthraquinone (2 moles) with benzidine


Cl
NHCO
CONH
Cl

(VI)



Algol Yellow GGC

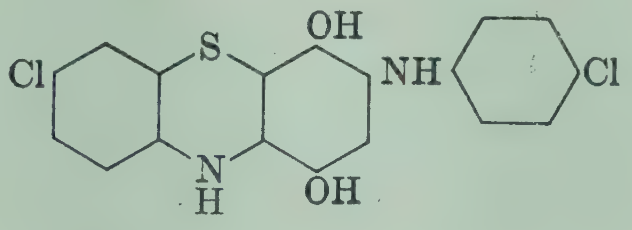


Indanthrene Yellow GF

(1 mole) and excess of sulfur at 250°. The finely divided product is oxidized with alkaline hypochlorite, yielding a bright and useful vat dye.[33] In light fastness (grade 5) it is better than Algol Yellow GC. Replacing benzidine by *p*-phenylenediamine, the product is Algol Yellow GR.[9] The structure assigned to Indanthrene Yellow GF needs to be confirmed since the analysis does not agree with the required values for carbon, hydrogen and sulfur.[11] The inferior light fastness of these dyes in comparison with most of the anthraquinone vat dyes is due to the thiazole ring system.

Derivatives of Diarylaminobenzoquinone

Thionation of 2,5-bis-*p*-chloroanilino-1,4-benzoquinone or Helindone Yellow CG (see Chapter XXVI) by means of aqueous sodium hydrosulfide, raising the temperature in steps to 135° and heating at this temperature (4 atms. pressure) for several hours, gives the thiazine derivative, Helindone Brown CV (IG) (CM, MLB; CI 1176).[34] Helindone Brown CV is a component of Helindone Black T and 3B.[35] Helindone Khaki C is prepared by thionating the same quinone with aqueous sodium sulfide in presence of ferric chloride at 140–145° under pressure.[35] Helindone Khaki CR is prepared by heating chloranil, aniline, sulfur and water at 165° under pressure. On wool, these Helindone dyes have excellent fastness to light (6–8) and milling (5).



Helindone Brown CV

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[33] Kalischer *et al.*, DRP 379,615.

[34] MLB, DRP 262,180; 281,520–1; 282,502–3; see also Brass, *Ber.* **45,** 2529 (1912).

[35] *BIOS* **1493.**

CHAPTER XXXVII

PHTHALOCYANINES

The formation of a blue pigment when a pyridine solution of phthalonitrile was heated with cuprous bromide was observed by de Diesbach and von der Weid,[1] who failed to appreciate the significance of their observation and to determine the chemical constitution of the pigment. It was noticed in 1928 by Dandridge, Dunworth, Drescher, and Thomas at the works of Scottish Dyes (part of ICI) that there was a dark blue impurity in phthalimide prepared by passing ammonia into molten phthalic anhydride in an iron vessel. The blue pigment was isolated and found to be a new type of organic iron compound with remarkable properties, and the observation resulted in the discovery of the phthalocyanines, which constitute a new, large, and outstandingly important group of synthetic coloring matters.[2, 3] Phthalocyanine is a composite word indicating the color of the substances and their derivation from phthalic acid. Compounds containing copper, nickel and other metals were soon prepared by the action of metals, oxides and salts on phthalamide and its dehydration products, and suitable methods were developed for their commercial production; the copper pigment (Monastral Fast Blue BS; ICI, 1934) is the most valuable member of the series. *o*-Cyanobenzamide and phthalonitrile combine with copper and copper salts very readily, and copper phthalocyanine is formed in quantitative yield from one atom of copper and four moles of phthalonitrile. The copper atom is held by the phthalocyanine molecule in very firmly bound chelate combination. As pigments, the phthalocyanines are characterized by the brilliance and beauty of the shades, high tinctorial power, and excellent fastness to light, heat, acid and alkali; and they are widely used for coloring paints, lacquers, printing inks, plastics, rubber, leather, cloth and other materials for which blues and greens of high fastness are desired. They can be used in calico printing by the pigment emulsion technique and in the mass pigmentation of rayon.[4]

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[1] *Helv. Chim. Acta* **10,** 886 (1927).

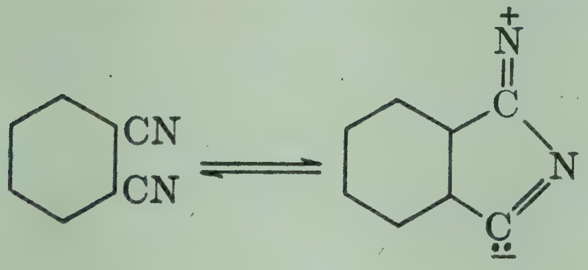
[2] Dandridge, Drescher, Thomas, and ICI, BP 322,169; Thorpe, Linstead, Thomas, and ICI, BP 389,842; Thorpe, Linstead, and ICI, BP 390,149.

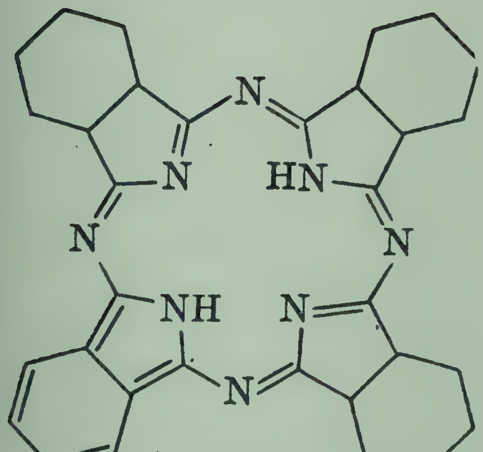
[3] For recent accounts of the chemistry and uses of the phthalocyanine coloring matters, see Haddock, *J. Soc. Dyers Colourists* **61,** 68 (1945); Haddock and Linstead, *in* Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. IX, Longmans, London, p. 617.

Heliogen Blue B (IG) is copper phthalocyanine, for which methods of preparation were independently evolved by the German group. There has since been a rapid succession of ICI and IG patents on the phthalocyanines; these have covered many modifications in manufacturing procedures and hundreds of derivatives, many of which have undoubted possibilities as dyes and pigments, obtained by halogenation, sulfurization and other treatments. The chlorinated phthalocyanines are blue-green and green pigments, and the sulfonic acids are water-soluble dyes applicable to textile fibers and in the preparation of lakes.

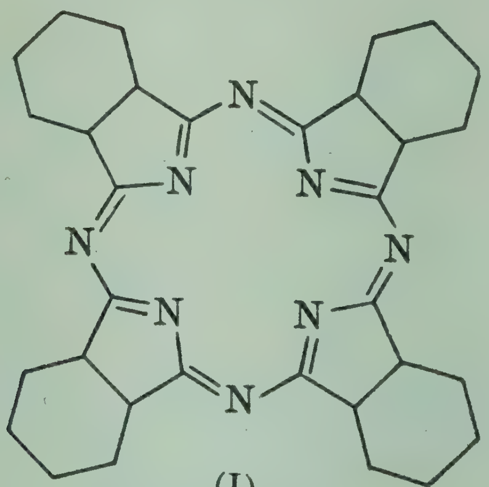
Properties and Chemical Constitution of the Phthalocyanines

The brilliant investigations of Linstead[3, 5] have established the constitution of the iron, copper and other metal phthalocyanines, and of the parent metal-free phthalocyanine, as molecules containing four *iso*indole units and as synthetic analogs of the naturally occurring porphyrins which are derived from the porphin ring system. A molecule of a phthalocyanine is produced from four molecules of phthalonitrile and two hydrogen atoms (or their equivalent of a metal) by the condensation of the *o*-dinitrile groups to a unique, strainless 16-membered ring system, identical with the porphin skeleton except for the replacement of four





(II)
Phthalocyanine
(Tetrabenzotetrazaporphin)
(Tetrabenzoporphyrazine)



(I)
Tetrabenzotetrazadehydroporphin
(Tetrabenzodehydroporphyrazine)

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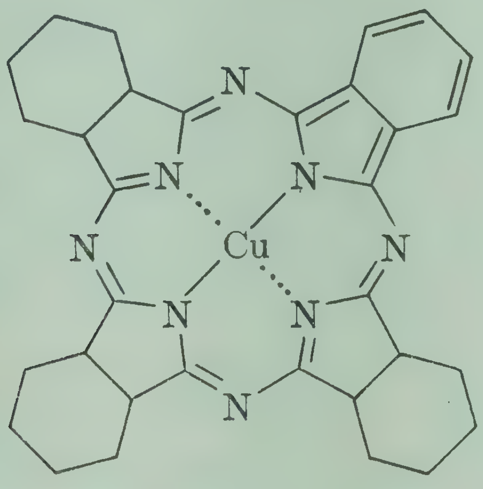
[4] See Chapter VI.

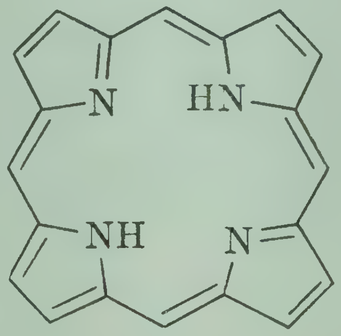
[5] See also *JCS* 1016 (**1934**); *Ber.* **72,** 93 (1939).

methine groups by nitrogen atoms.[6] Phthalonitrile may be assumed to react in the polar isoindole structure, as indicated. Elementary analysis does not distinguish between tetrabenzotetrazadehydroporphin (I) and the accepted constitution (II) of the parent metal-free phthalocyanine. The correctness of the latter, which has two more hydrogen atoms, was shown by the action of ceric sulfate;[7] phthalocyanine consumes one atom of oxygen per mole, forming 4 moles of phthalimide and 4 moles of ammonia, in accordance with the equation: $(C_8H_4N_2)_4H_2 + 7H_2O + [O] \rightarrow 4C_8H_5O_2N + 4NH_3$. The dehydroporphin structure should undergo hydrolytic fission without consuming oxygen: $(C_8H_4N_2)_4 + 8H_2O \rightarrow 4C_8H_5O_2N + 4NH_3$. The molecular weight of magnesium phthalocyanine, determined ebullioscopically, is in agreement with the substitution of two hydrogen atoms by one of magnesium in the indicated structure for phthalocyanine.[8]

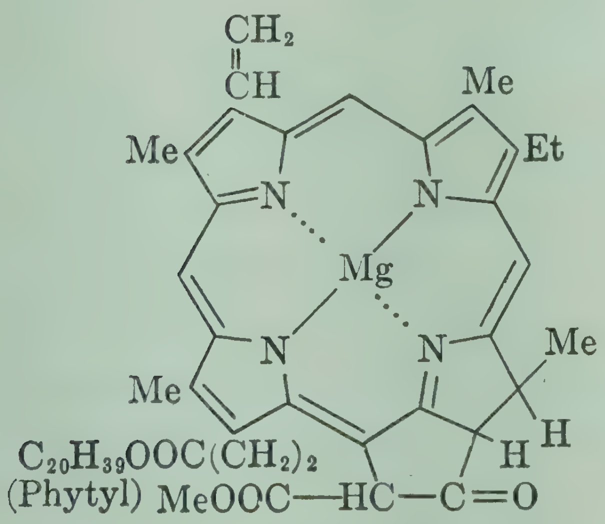
The phthalocyanines are closely related in structure to chlorophyll, the pigment of green leaves, and hemin, the pigment which in association



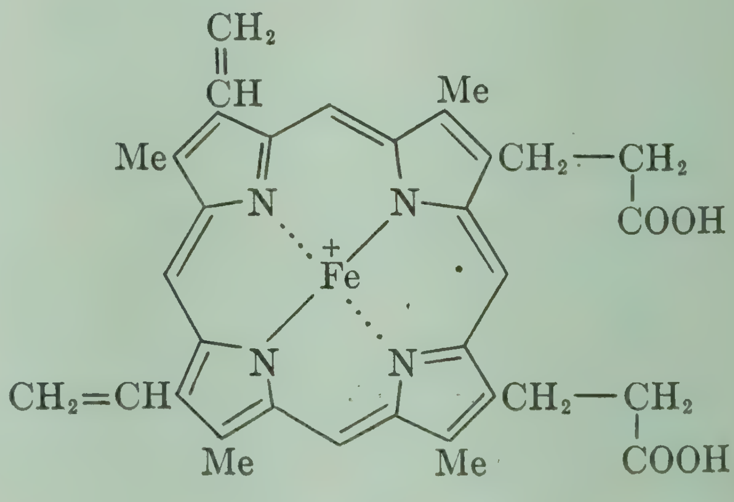
Copper phthalocyanine



Porphin



Chlorophyll-a



Hemin

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[6] For a study of the m.w. of phthalocyanine in sulfuric acid, see Sirur *et al.*, *Proc. Natl. Inst. Sci. India* **13,** 141 (1947).

[7] Dent, Linstead, and Lowe, *JCS* 1033 (**1934**).

[8] Linstead and Lowe, *JCS* 1031 (**1934**).

with protein is hemoglobin, the coloring matter of mammalian blood. Numerous porphyrins[9] also occur in the animal and vegetable kingdom; in the human organism some appear under pathological conditions. Porphyrins derived from chlorophyll have also been detected in oil shales, petroleum, coal and other minerals, and their instability at relatively high temperatures has assisted geological speculations.[10]

Intense color and great stability are two striking properties of both the natural porphin derivatives and the synthetic phthalocyanines. Although the natural porphyrins undergo certain changes by mild treatments, these are minor alterations by which the side chains are affected, and the skeletal ring system exhibits remarkable resistance to degradation. The hard framework in each case is an aromatic system stabilized by resonance among numerous structures. The phthalocyanines are highly crystalline, vary in color from reddish blue to bluish green, and are extremely stable. Copper phthalocyanine for instance sublimes without decomposition at 550–580°, dissolves in concentrated sulfuric acid and is recovered unchanged on dilution. When a concentrated sulfuric acid solution of magnesium phthalocyanine is diluted, the metal is removed, but the ring system is intact and the product is phthalocyanine itself. An important property of the phthalocyanines is the comparative ease with which they undergo substitutions in the four benzene rings. Thus by direct chlorination in molten sodium-aluminum chloride or phthalic anhydride, all the sixteen available positions can be substituted by chlorine atoms; the pentadecachloro compound is a valuable technical product. The phthalocyanines can also be sulfonated readily, but they are decomposed by nitric acid and cannot be nitrated. The aromatic character of the phthalocyanine system is further shown by its magnetic anisotropy, which is about 15 times as large as that of benzene.[11] Another notable characteristic of the phthalocyanines is the ease with which the formation of these molecules containing a very complex ring system takes place; so great indeed is the tendency for phthalodinitrile, and even phthalamide, to form the metal phthalocyanines that they were probably encountered as by-products in reactions involving phthalamide and its derivatives many years before their significance was realized by the ICI group of workers.

The phthalocyanines are all insoluble in water, and the metal phthalocyanines belong to two types which differ in some of the other properties.[12] One type is represented by the sodium, potassium, calcium, barium, and cadmium compounds; and the second by the derivatives of other metals. The first type would appear to be electrovalently linked salts, being insoluble in organic solvents, nonvolatile at high temperatures in a vacuum and readily decomposable to metal-free phthalocyanine by means of acids or even water. The second type comprises coordination compounds, which are moderately soluble in boiling solvents such as chloronaphthalene and quinoline, sublime without decomposition at or below 600° *in vacuo*, and are very stable to hydrolytic treatments. The stability to acid reaches a maximum with the phthalocyanines derived from metals (e.g., copper, zinc, iron, cobalt, and platinum) whose atomic radii fit reasonably well into the center of the phthalocyanine molecule; when the atomic radii of the metals (e.g., manganese and lead) are considerably larger or smaller than 1.35 A, the metal atoms are more readily removable from the phthalocyanines,[12] and they vary from complete insolubility to moderate solubility in boiling chloronaphthalene, quinoline and other high boiling organic solvents. Some sublime *in vacuo* at temperatures up to 600° without decomposition, and some do not sublime at all.

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[9] Fischer, *Ber.* **60**, 2611 (1933).

[10] Treibs, *Angew. Chem.* **49**, 682 (1936).

[11] Lonsdale, *Proc. Roy. Soc. London* **A159**, 149 (1937).

[12] Barrett, Dent, and Linstead, *JCS* 1725 (**1936**).

An interesting property of the metal phthalocyanines, particularly iron phthalocyanine, is their ability to catalyze oxidations; thus benzaldehyde can be oxidized to benzoic acid, and diphenylmethane to benzophenone, by air in presence of phthalocyanine.[13] Ferrous phthalocyanines in dyestuff printing pastes improve the rate of development, especially of indigoid, thioindigoid and halogenated anthanthrone dyes.[14]

The constitution assigned to the phthalocyanines by chemical evidence has been confirmed by X-ray spectrography. The crystal structure of the phthalocyanines shows the presence of approximately square flat molecules having a center of symmetry.[15] This center may be occupied by two hydrogen atoms or by the metals nickel, copper or platinum without distortion of the crystal lattice; the four valencies of the metal must be coplanar. The derivatives of 4-coordinate beryllium, manganese, iron, and cobalt also exhibit planar symmetry in the crystals.[16] In view of the tetrahydral symmetry of cobalt in the group $CoCl_4''$ and of beryllium in various derivatives, the planar configuration of the cobalt and beryllium phthalocyanines points to the structural stability of the framework of the phthalocyanine molecule which makes the metals conform to its steric requirements. The crystals of the various metal phthalocyanines are very closely isomorphous, and the entry of a metallic atom has hardly any effect on the size of the molecule. Haurowitz[17] has found that the metallic derivatives of the porphyrins have practically the same dimensions as the metal-free porphyrins.

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[13] Cook, *JCS* 1761, 1768, 1845 (**1938**); Tamamushi and Tohmatsu, *Bull. Chem. Soc. Japan* **15,** 223 (1940).

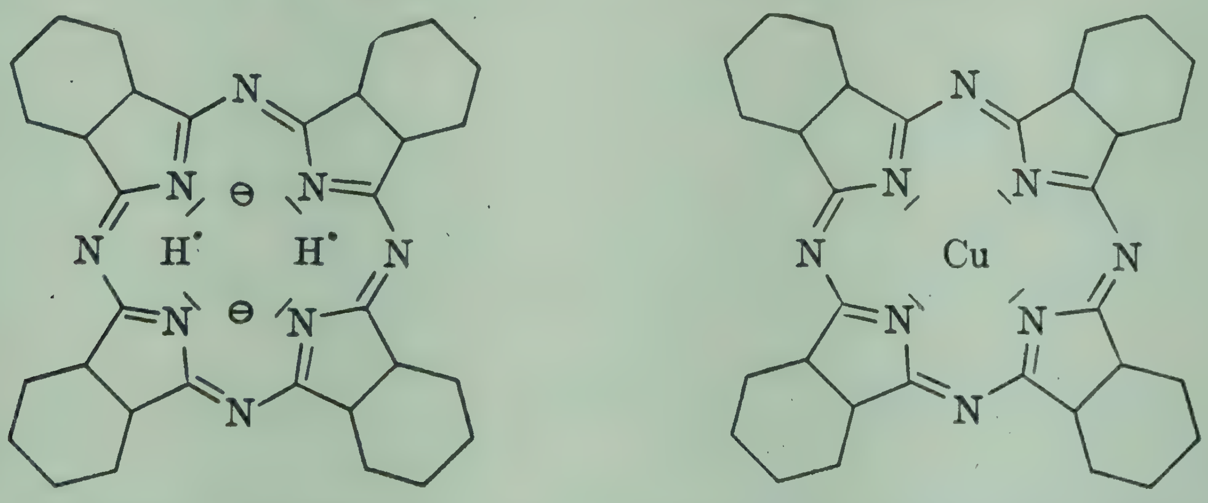
[14] Chapman *et al.* and ICI, BP 526,823.

[15] Robertson, Linstead, and Dent, *Nature* **135,** 506 (1935); Robertson, *JCS* 615 (**1935**).

[16] Linstead and Robertson, *JCS* 1736 (**1936**).

In his work on the phthalocyanines Robertson[18] accomplished the first direct X-ray analysis of an organic molecule, not even involving the assumption of the presence of discrete atoms. This was possible because of the crystallization of phthalocyanine in a molecular arrangement having centers of symmetry at which different metal atoms can be inserted by means of chemical reactions without appreciable alteration in the crystal structure. The X-ray contour diagram, showing the electron distribution in the molecule, has not merely confirmed Linstead's structure for phthalocyanine, but has also indicated the additional regularity of a complete resonance system. The measured bond distances give no indication of *o*-quinonoid structures or of the fixation of one of the Kekule structures in the benzene rings as a result of fusion with the 5-membered rings. There is a slight departure from tetragonal symmetry in the molecule as a whole, because the central nitrogen atoms are drawn closer together along two out of the four possible lines of hydrogen bond formation. In the metal phthalocyanines the dimensions of the molecule are very similar for the several compounds examined, with slight variations in the nitrogen-metal distances due to the differences in the radii of the atoms. Thus the nitrogen-metal distance in platinum phthalocyanine is 2.01 A as compared with 1.92 A and 1.83 A in the metal-free and the nickel compound respectively.

On the basis of a recent study of the electron density contour patterns of the natural porphyrins, the phthalocyanines, and a series of azaporphines, Endermann represents the high degree of symmetry in the phthalocyanines by the appended structures (III) and (IV).[19]



(III)

(IV)

Electronic formulas for Phthalocyanine and Copper phthalocyanine (Endermann)

[17] Haurowitz *et al.*, *Ber.* **68,** 1795 (1935).

[18] Robertson *et al.*, *JCS* 1195, 1736 (**1936**); 219 (**1937**); 36 (**1940**).

[19] Endermann, *Z. physik. Chem.*, **190,** 129 (1942).

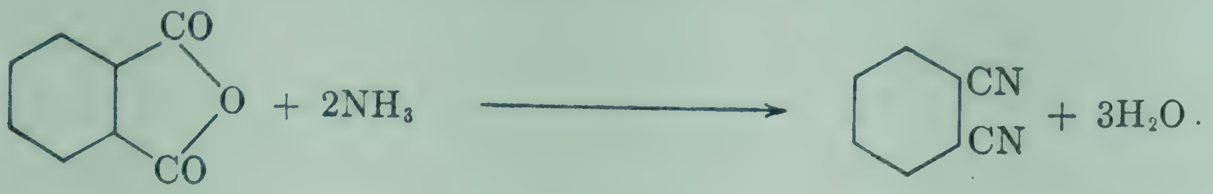
While 1,2- and 2,3-dicyanonaphthalenes yield the corresponding naphthalocyanines, which are a rather dull green in color, 1,8-dicyanonaphthalene does not undergo the phthalocyanine reaction, which is in conformity with the constitution of the phthalocyanines.[20] Phthalocyanines in which the four benzene rings are replaced by heterocyclic ring systems have been prepared, e.g. tetrathiopheno-, tetrathionaphtheno-, tetrapyridino- and tetrapyrazinoporphyrazine.[21] Attempts to prepare analogs from pyrrole, furan, isotriazole and isoxazole have been unsuccessful, and the failure is explicable when the bond arrangements in these rings and the aromatic character of the phthalocyanines are considered. Phthalocyanine analogs in which one, two, three and four of the aza-nitrogen atoms are replaced by methine groups have been synthesized; they are bright green in color, as fast to light as the phthalocyanines, and more stable towards oxidation.

PHTHALONITRILE

Phthalonitrile (needles from water, m.p. 141°) is the principal intermediate for phthalocyanine manufacture, and processes for continuous catalytic production from phthalimide, phthalamide, and phthalamic acid have been developed. The vapors of one of these compounds, together with ammonia, may be passed over selected catalysts such as the phosphates of aluminum, magnesium, zirconium or thorium, or aluminum silicate, arsenate, arsenite, or borate.[22] The amides may be dehydrated under pressure with acid halides and an acylated secondary amine and, if necessary, a tertiary base and a solvent; thus *N*-ethyl formanilide may be employed with phosgene, sulfuryl chloride or phosphorus trichloride.[23] The preparation of phthalonitrile by catalytic dehydration of phthalimide or ammonium phthalate is described by du Pont,[24] a basic aluminum phosphate catalyst being used at 300–550°; Ciba employ a phosphorus or sulfur halide or an organic acid halide with an acid-binding agent and an inert solvent.[25] Phthalonitrile is obtained from phthalimide by treatment with phosgene in pyridine or dimethylaniline.[26] When the gaseous catalyzed reaction product from phthalic anhydride and ammonia is sprayed with very cold water, a slurry is obtained from which the nitrile can be separated.[27]

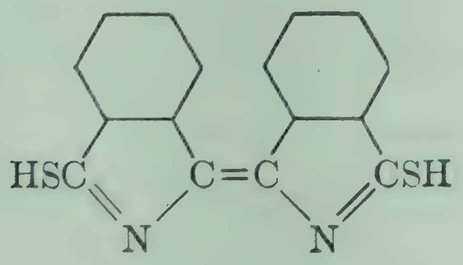
[20] Bradbrook and Linstead, *JCS* 1744 (**1936**).
[21] Linstead, Noble, and Wright, *JCS* 911 (**1937**); Bilton and Linstead, *ibid.* 922 (**1937**).
[22] Ciba, BP 526,234.
[23] Geigy, BP 532,516.
[24] du Pont, BP 515,192.
[25] Ciba, BP 519,888.
[26] Davies, Jones, and ICI, BP 441,399.
[27] Bowlus and du Pont, USP 2,232,836.

Details of the plant and process for phthalonitrile at IG Ludwigshafen have been described.[28] The overall reaction is



Ammonia at 340° enters molten phthalic anhydride. The resulting mixture of phthalic anhydride vapor or its reaction product with ammonia is heated to 400–430°, and is led from below into a contact chamber (about 1000 l. effective volume) containing a bauxite catalyst. The reaction is endothermic, and the chamber is electrically heated. The reaction gases (phthalonitrile + steam + excess ammonia) are cooled to about 210° and blown into a cold atmosphere of ammonia in large aluminum separators, so that the phthalonitrile is cooled quickly below its melting point. About 90% of the total phthalonitrile separates at this stage as a fine, light yellow powder, and more (making up a total yield of 91–92%) is recovered by settling in a series of chambers and by filtering the gas stream. After drying at 55–60°, the purity of the phthalonitrile is 89.8–91.7%.

Phthalonitrile undergoes an interesting reaction with hydrogen sulfide in alcoholic solution, forming (V), which may be converted into mono- or dialkyl thioethers.[29] These condense with compounds having a reactive methylene group to form colored derivatives suitable for use as pigments or vat dyes, or wool dyes after sulfonation. For instance, α-naphthol gives a greenish-blue vat dye, 4,5-benzothioindoxyl a green vat dye, and 1-phenyl-3-methyl-5-pyrazolone a violet vat dye. With arylamines, one or both of the alkylthiol groups are replaced, forming pigments or dyes for wool or acetate rayon. The dianilino derivative is brown; the color is lightened by substituents to red, orange, and yellow.[30]



(V)

Metal-Free Phthalocyanine

Metal-free phthalocyanine is best prepared by the removal of metal from suitable metal phthalocyanines. The metal can be eliminated from lead, tin, and manganese phthalocyanine by means of 100% sulfuric acid,[31] but disodium phthalocyanine is smoothly converted into phthalocyanine by merely stirring with cold methanol.[32] Metal-free phthalocyanine (Heliogen Blue G) is prepared by IG from the sodium compound, which is obtained by dissolving sodium metal (28 kg.) in Intrasolvan HS (a mixture of isohexyl and isoheptyl alcohol, b.p. 145–155°) at 60°, adding phthalonitrile (256 kg.), and heating at 145–150° for 5 hours. The product is filtered off from the hot solvent, and freed from metal by grinding with methanol at 20° for 6 hours in a turbo mixer. Sodium-free phthalocyanine is collected in a closed filter press and washed with methanol and water till alkali-free. The yield is quantitative.[38]

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[28] *BIOS* **986.**

[29] Drew, Kelly, and ICI, BP 516,342.

[30] Davies and ICI, BP 517,630; 519,064.

Phthalocyanine is formed when phthalonitrile is heated in a sealed glass vessel at 350–360°.[33] The two additional hydrogen atoms necessary for the tetramerization of phthalonitrile to phthalocyanine have to be provided by the decomposition of phthalonitrile itself, or various substances may be added for fulfilling this purpose and as promoters for the reaction. Among the many substances which have been suggested are acid amides,[34] triethanolamine,[35] phenols, naphthols, or aliphatic hydroxy compounds.[36] In heating phthalonitrile or one of its derivatives with a caustic alkali to make metal-free phthalocyanines, the addition of methylglucamine is an advantage.[37]

Chlorination of phthalocyanine until 14–15 atoms of chlorine are introduced can be effected in molten phthalic anhydride (10 parts) containing antimony trisulfide (0.15 part) at 155–160°. The product is purified by dissolving in chlorosulfonic acid and monohydrate, and precipitating with water. IG market the product as Heliogen Green GG.[38]

Preparation of the Metal Phthalocyanines

Phthalocyanines have been prepared from metals which belong to every group of the periodic table. Listed according to the groups, they are (I) Li, Na, K, Cu, Ag; (II) Be, Mg, Ca, Ba, Zn, Cd, Hg; (III) Al; (IV) Sn, Pb; (V) V, Sb; (VI) Cr, Mo; (VII) Mn; (VIII) Fe, Co, Ni, Pd, Pt. The color of the metal phthalocyanines varies from reddish blue to green; the copper compound is the reddest in shade, which becomes progressively greener in the order nickel, cobalt, metal-free, zinc, aluminum, beryllium, tin, and lead phthalocyanine.

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[31] Byrne, Linstead, and Lowe, *JCS* 1020 (**1934**).

[32] Dent and ICI, USP 2,214,454.

[33] Heilbron, Linstead, Thorpe, and ICI, BP 410,814.

[34] IG, BP 457,526.

[35] Lowe and ICI, BP 460,594.

[36] IG, DRP 696,334.

[37] Palmer, Gross, and du Pont, USP 2,413,191.

[38] *BIOS* **960.**

In a general study of the behavior of phthalocyanine as a chelating group, Linstead employed three main methods for the preparation of the derivatives of nineteen metals. Various modifications have been described in the patent literature (see later under copper phthalocyanine).

(1) Phthalocyanine itself yields metal phthalocyanines on heating with metals or suitable soluble salts in high boiling solvents.

(2) The most general method is the interaction of a metal or its salt with phthalonitrile or an analogous *o*-dinitrile derived from a dicarboxylic acid which readily forms the anhydride. When phthalonitrile is heated with free metals such as zinc, the metal phthalocyanine is formed by the simple reaction:

$$4C_6H_4(CN)_2 + Zn \rightarrow C_{32}H_{16}N_8Zn.$$

Calcium phthalocyanine is of interest for its ready convertibility into other metallic derivatives. The antimony compound is exceptional, possessing the formula $(C_{32}H_{16}N_8)Sb_2$. The space available in the center of the phthalocyanine molecule will not permit the packing of two antimony atoms, and in order to satisfy the ordinary valency requirements of antimony, it is necessary to assign to the compound a structure such as $(C_{32}H_{16}N_8){=}Sb{-}Sb{=}Sb{-}Sb{=}(C_{32}H_{16}N_8)$, in which each of the two terminal antimony atoms is located in the center of a phthalocyanine molecule.[39] Magnesium naphthalocyanine is an interesting substance, which is readily soluble in cold ether.[20]

When metallic chlorides are used, a benzene ring may be chlorinated; while phthalonitrile gives copper phthalocyanine with cuprous chloride below 200°, the product formed above this temperature in presence of cupric chloride is copper 4-monochlorophthalocyanine: $4C_6H_4(CN)_2 + CuCl_2 \rightarrow C_{32}H_{15}ClN_8Cu + HCl$. An additive reaction might take place, the halogen remaining attached to the metal; thus stannous chloride and phthalocyanine react violently to form dichloro-tin phthalocyanine: $4C_6H_4(CN)_2 + SnCl_2 \rightarrow C_{32}H_{16}N_8SnCl_2$. Both these processes may be involved:

$$4C_6H_4(CN)_2 + AlCl_3 \xrightarrow{250°} C_{32}H_{15}ClN_8AlCl + HCl.$$

Stannic chloride behaves similarly, giving dichloro-tin chlorophthalocyanine. Magnesium chloride and antimony pentachloride do not react with phthalonitrile. The action of aluminum chloride, stannous chloride and stannic chloride are of special interest, since the phthalocyanines contain electrovalently attached chlorine. On treatment with alkali, the electrovalently bound chlorine can be replaced by hydroxyl, while the nuclear chlorine, if present, is unattacked. When dichloro-tin phthalocyanine, the product of the reaction between stannous chloride and phthalonitrile, is reduced with hydrogen, stannous phthalocyanine, which is also formed by the interaction of metallic tin and phthalonitrile at 300°, is obtained. By the interaction of dichloro-tin phthalocyanine and disodium phthalocyanine in boiling chloronaphthalene, the product is stannic phthalocyanine, $Sn(C_{32}H_{16}N_8)_2$, which is unique among the metallic phthalocyanines in containing two phthalocyanine units attached to one atom of metal.[12]

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[39] Barrett, Frye, and Linstead, *JCS* 1157 (**1938**).

Using metallic oxides (e.g. litharge, sodium amyloxide), the reactions are more complex.

(3) *o*-Cyanobenzamide, heated with a metal, undergoes dehydration and combination with the metal: $4C_6H_4(CN){-}CONH_2 + Ni \rightarrow C_{32}H_{16}N_8Ni + 4H_2O$. Although this method gives lower yields than the phthalonitrile reaction, it is useful in special cases; e.g. magnesium oxide gives a good yield of the corresponding phthalocyanine when *o*-cyanobenzamide is used.

(4) A further method due to Wyler, which has technical value and of which details are given later, is to heat phthalic acid, anhydride or imide with urea and a metal or metallic salt.

Derivatives of phthalic acid and its nitrile, which are difficult or impossible to obtain by direct substitution, can be prepared from appropriate intermediates, e.g. the *o*-dichloro-compounds; they may then be utilized for preparing nuclear substituted phthalocyanine pigments which are not accessible by direct substitution of the phthalocyanines. Examples of such derivatives are acetamido;[40] benzoyl and naphthoyl;[41] phenyl;[42] alkyloxy and aryloxy;[43] benzoxazyl, benzothiazyl and benzimidazyl.[44] The derived phthalocyanines can be sulfonated and used as dyes or as color lakes.[45]

Copper Phthalocyanine and Its Derivatives

The most important phthalocyanine pigment is the copper compound (Monastral Fast Blue BS, ICI; Heliogen Blue B and N, IG), and the principal method of manufacture is from phthalonitrile; IG used a phthalic anhydride-urea condensation when there was a shortage of

[40] IG, BP 481,134.
[41] IG, BP 468,043.
[42] IG, BP 470,542.
[43] IG, BP 470,703.
[44] IG, BP 488,201.
[45] IG, BP 491,151.

phthalonitrile.[38, 46, 47] Phthalonitrile (4 moles) and cuprous chloride (1 mole) are heated together at the melting point of the nitrile (141°); the reaction is exothermic, the temperature rising to 260–300°, and it is complete in under an hour. A 92.5% yield is obtained. A continuous process recently used by IG has been described,[38] in which a mixture of the nitrile (4 moles) and cuprous chloride (1.2 moles) is fed on to a rotating continuous metallic band, heated electrically, permitting a sensitive control of the temperature. The band is enclosed in a jacket under slight nitrogen pressure. At the rear of the band, the product falls on to a crusher.

In the urea-solvent process, phthalic anhydride (373 kg.), urea (600), cuprous chloride (70) and arsenic pentoxide (10 kg.) in trichlorobenzene are heated to 160° in a reaction vessel provided with an agitator. Anhydrous ferric chloride (alone or mixed with aluminum chloride) can replace arsenic oxide. When the vigorous reaction has subsided, the mixture is heated at 200° for 5 hours; trichlorobenzene distils over continuously. The residue is then diluted with hot trichlorobenzene, filtered, and washed with trichlorobenzene. The cake is freed from solvent in a dryer, washed with dilute hydrochloric acid by stirring for 1 hour at 96°, filtered, washed and dried (yield 343 kg., calculated as 100% copper phthalocyanine).

The crude copper phthalocyanine prepared by these methods is purified by dissolving the powdered material in 96% sulfuric acid and precipitating by the addition of hot water. The precipitate is collected, washed with ammonia, made into an 18% aqueous paste with the aid of a dispersing agent (e.g. Emulphor FM, the monooleic ester of triethanolamine) and dried to a fine powder. This is marketed as Heliogen Blue B or N according as the phthalonitrile or the urea process has been used. The concentrated sulfuric acid treatment converts the β-modification of Heliogen Blue to the color-valuable α-modification; attempts to replace the concentrated sulfuric acid treatment by a process of grinding with salt have not proved practicable. Heliogen Blue BT, Vulcan Fast Blue 5G (for rubber), Heliogen Blue BK, and Heliogen Blue NCB (for nitrocellulose lacquer) are IG brands of copper phthalocyanine, which differ in the percentage content of the pure pigment, the physical state and the special purpose for which the product is intended.

Lecher, Lacey, and Orem[48] have observed that pure cuprous halides or copper powder do not react with phthalonitrile in boiling pyridine if air is excluded. Oxygen oxidizes cuprous halides dissolved in pyridine.

[46–47] For a detailed account of IG methods of preparation of phthalocyanine pigments and dyes, see Ref. 38; (46) *FIAT* **1309**; (47) *FIAT* **1313** III, pp. 273–347.

[48] *JACS* **63**, 1326 (1941).

Cupric halide-pyridine complexes precipitate and a colloidal solution of cupric oxide is formed; cupric oxyhalides might also be present. Oxygen oxidizes copper powder suspended in boiling pyridine. The conversion of phthalonitrile into copper phthalocyanine in boiling pyridine requires cupric compounds, preferably in the presence of a mild reducing agent such as cuprous halide or copper. Cuprous halides in the presence of oxygen are reactive. So are finely dispersed cupric oxide, cupric oxyhalides or mixtures of cupric halides and cupric oxide. In the absence of any reducing agent part of the pigment formed assumes this function.

The purity of a sample of phthalonitrile can be estimated by taking advantage of the quantitative conversion of the nitrile to copper phthalocyanine under specified conditions. Thus the nitrile (51.2 g.), nitrobenzene (350 cc.), cuprous chloride (20 g.) and pyridine (16 g.) are heated at 190–200° for 1.5 hours. Part of the nitrobenzene (200 cc.) is distilled off; the precipitate filtered hot and washed with hot nitrobenzene and with methanol till the filtrate is colorless, then extracted with hot 5% hydrochloric acid, refiltered, washed successively with water, methanol and acetone, dried and weighed.[47]

Heliogen Green B is copper tetraphenylphthalocyanine, prepared by heating a mixture of pyridine (8 parts), cuprous chloride (19.5), 3,4-dicyanodiphenyl (80) and *o*-dichlorobenzene (390) at 176–178°. This pigment has a distinctly bluer and somewhat clearer shade than Heliogen Green G, the two being equivalent in fastness properties.[49]

Modified methods of preparation of copper phthalocyanine. Although copper phthalocyanine can be readily prepared by heating phthalonitrile and copper or a copper salt together, numerous modifications in the preparation of copper phthalocyanine, as well as the other metal phthalocyanines, have been suggested in the patent literature. The use of diluents or acid amides[34] or tertiary bases[50] is said to be an advantage. A large quantity of inert material such as common salt added to the reaction mixture serves to control the temperature of the strongly exothermic reaction.[51] A mixture of an aromatic *o*-dinitrile and an alkali or alkali earth amide or cyanamide in an organic diluent free from hydroxyl and mercapto groups is warmed, and an alcohol, mercaptan or phenol is then added.[52] When the reaction is carried out in an organic solvent (e.g. nitrobenzene), alkali oxides, hydroxides, and carbonates in small amounts act as promoters.[53] Copper phthalocyanine may be prepared from phthalonitrile, which may contain phthalamide, by treatment with a cupric salt and ammonia in an inert diluent at 180–220°.[54] The phthalocyanine condensation may be effected in ethylene glycol at 137–140°, trimethylene glycol at 165–170°, or butyl carbitol at 225°.[55] Phthalonitrile vapor may be brought into contact with a copper surface at 225–230° and the pigment removed with a scraper, thus exposing a fresh surface.[56] Good agitation of the melt is obtained by carrying out the reaction between phthalonitrile and copper piecemeal in the same vessel at 220–225°, adding the two reactants in successive batches, after each batch has been converted, until the vessel is full. Ammonium chloride, stannous and stannic chlorides, antimony and aluminum trichlorides, and cuprous chloride act as catalysts, enabling the reaction to be initiated and completed at 180°.[57] The reaction may be carried out in trays with infrared rays as the source of heat, a method which du Pont describe for a variety of metallic phthalocyanines as well as for sulfur dye melts and the conversion of arylamine sulfates into *p*-aminoarylsulfonic acids.[58]

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[49] *BIOS* Misc. Report **20.**

[50] IG, BP 458,780.

[51] IG, FP 799,901.

[52] IG, DRP 741,251.

[53] Ciba, BP 538,957.

Phthalonitrile may be formed *in situ* by heating *o*-chloro or *o*-bromobenzonitrile with cuprous cyanide;[59] better yields are obtained by the addition of metallic copper.[60] *o*-Dichloro or dibromo compounds can be used in the same manner in presence of organic nitrogenous bases.[61]

The urea process of Wyler[62] has the advantage over the phthalonitrile method that it involves the use of the readily accessible phthalic acid, anhydride and imide. The yields are much improved by the addition of boric acid and ammonium molybdate or other compounds of the V or VI groups.[63] According to Haddock[3] and contrary to Sander,[64] iminophthalimide is formed as an intermediate product, since the interaction of phthalic anhydride and urea, in presence of ammonium molybdate and in the absence of a metal, gives a good yield of iminophthalimide. The latter then undergoes dehydration to phthalonitrile.

Phthalic anhydride, a metal phthalate, urea and a naphthalenesulfonic acid (which prevents hardening of the reaction products) may be heated

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[54] Fairweather and American Cyanamid, BP 559,247; American Cyanamid, USP 2,302,612; 2,318,783; 2,318,787.

[55] Turek and Interchemical Corp., USP 2,138,413.

[56] Turek and Interchemical Corp., USP 2,245,098.

[57] du Pont, USP 2,160,837.

[58] du Pont and ICI, BP 552,124.

[59] Linstead *et al.* and ICI, BP 418,367.

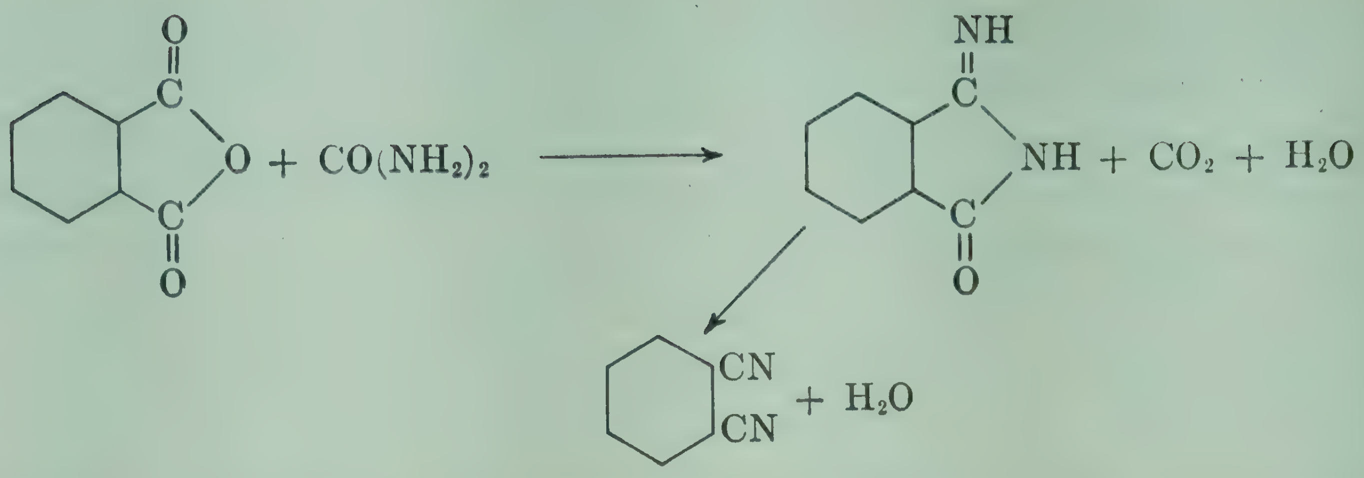
[60] Montecatini, BP 498,831.

[61] IG, BP 490,744–5.

[62] Wyler and ICI, BP 464,126.

[63] Riley and ICI, BP 476,243. See also Moser, USP 2,469,663; O'Neal, BP 633,713.

[64] *Die Chemie* 225 (1942).



together.[65] Instead of urea, an aminosulfonic acid,[66] dicyandiamide[67] or *p*-toluenesulfonamide can be used.

Chlorination of copper phthalocyanine. As many as 15–16 chlorine atoms can be introduced into phthalocyanine by direct chlorination, and the reaction is technically important for copper phthalocyanine because of the beauty and fastness of the green pigment thus obtained.[67a] The 4- and 5-positions in the benzene ring are first substituted, and these have little effect on the color; the octachloro compound is still blue. Substitution in the 3- and 6-positions has a bathochromic effect, as shown by the green color of the copper octachlorophthalocyanine, made synthetically from 3,6-dichlorophthalic acid. In the manufacture of the valuable green pigment by chlorination of copper phthalocyanine, the reaction is continued until 15–16 atoms of chlorine have been introduced. Various solvents have been suggested, and among those used technically are (1) a mixture of fused aluminum chloride and sodium chloride, and (2) molten phthalic anhydride. Aluminum chloride (924 parts) and dry rock salt (194) are melted together at 170°, and copper phthalocyanine is stirred in at 155–165°. Chlorination is commenced at the same temperature and proceeds without external application of heat, but towards the end of the reaction, which takes about 20 hours, the mixture may be heated at 180–190°. The hot melt is poured into water, a little hydrochloric acid added, the mixture agitated for two hours, and the product filtered, washed and dried.[38] IG market the product containing 15 atoms of chlorine per mole of copper phthalocyanine as Heliogen Green G. Like the parent pigment, the chlorinated compounds can be purified by dissolving in concentrated sulfuric acid and precipitating with water. Chlorination of copper phthalocyanine in acid chlorides, particularly phthalyl chloride, gives quantitative yields of products of high purity, color value and softness in the powdered state. IG have developed a pressure chlorination method in which the pigment (2 kg.) and antimony trisulfide (0.06) are suspended in carbon tetrachloride in an autoclave, and chlorine is led into the mixture maintained at 150–180°.[47] Copper hexadecachlorophthalocyanine can be prepared by heating tetrachlorophthalic anhydride (17), urea (63), ammonium molybdate (0.1) and cuprous chloride (4.3) in nitrobenzene at 150–230° until condensation is complete.[68]

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[65] Jaffe, BeP 450,302; 450,362; 450,950.

[66] Wyler and ICI, BP 457,786.

[67] Montecatini, BP 503,029.

[67a] Sulfur dichloride in presence of iron and/or antimony trichloride can be used for the production of phthalocyanines containing about 50% chlorine; du Pont, USP 2,377,685.

The chloro derivatives of copper and other phthalocyanines, in addition to their importance as pigments, are of interest as intermediates for the preparation of other derivatives (e.g. aryloxy-, alkylamino- and arylaminophthalocyanines) by replacement of the chlorine atoms.[69] Pigments for paper are prepared by heating chlorinated phthalocyanines with a thiol (e.g. thiophenol) in an alcohol of b.p. $> 150°$ and in presence of alkali.[70]

Fluorination of a variety of hydrocarbons, intermediates and dyes in hydrogen fluoride solution or suspension has been described;[71] and up to seven atoms of fluorine per mole have been introduced into the phthalocyanines.[72]

The phthalocyanines as pigments. In view of their brilliance and stability, the phthalocyanines are especially valuable as pigments; but among the many hundred phthalocyanine derivatives which have been described, there are only three which are extensively used for coloring printing inks, paints, varnishes, enamels, plastics, and other materials. These are metal-free phthalocyanine (Monastral Fast Blue G, ICI), copper phthalocyanine (Monastral Fast Blue B) and highly chlorinated copper phthalocyanine (Monastral Fast Green G). As usual, the physical form of the pigments is an important consideration, and much attention has been paid to methods by which the phthalocyanine pigments can be produced in a state of dispersion in which they have the maximum brightness, color value and covering power.[47] The pure, highly crystalline compounds are valueless as pigments. A general method is to dissolve the pigment in concentrated sulfuric acid and drown the solution in water or a solution of a dispersing agent such as an alkylnaphthalenesulfonic acid-formaldehyde condensation product; and various details for such treatments are mentioned in patents.[73] The strength and brilliance of shade of phthalocyanines, as well as anthraquinone and thioindigo vat dyes, are increased by dilution of a sulfuric acid solution of the pigment with water in a state of turbulent flow.[74] The phthalocyanine is dissolved in fused naphthalene-2-sulfonic acid (or concentrated phosphoric acid) and poured into water.[75] To secure better dispersibility in rubber, the phthalocyanines are dissolved in sulfuric or phosphoric acid together with a fatty acid of not less than 12 carbon atoms, drowned in hot water and worked up.[76] The pigments may be finally milled or ground in the presence of water-soluble dispersing agents such as sulfonated oils or sulfated higher fatty alcohols. Fine-textured phthalocyanine pigments, capable of forming stable uniform dispersions in paint, lacquer, or varnish vehicles, can be prepared by incorporating aluminum benzoate, or sodium benzoate and aluminum sulfate, in the wet pigment paste and drying the mixture.[77] In the preparation, storage and use of phthalocyanine dispersions it is necessary to keep in view the great tendency for the phthalocyanines to revert to the crystalline state. Pigments of "outstanding brilliance and color stability" are obtained by blending blue phthalocyanines with yellow α-aroylamidoanthraquinones; the tinctorial value is greater than that calculable from the individual pigments.[77a]

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[68] Sandoz, BP 585,727.

[69] IG, BP 469,139; 471,435.

[70] Sandoz, BP 588,231; 629,488; USP 2,456,274.

[71] du Pont, USP 2,013,030.

[72] du Pont, USP 2,227,628.

[73] E.g. Davies, Hailwood, Todd, and ICI, USP 2,213,693; du Pont, BP 547,411; Montecatini, BP 502,623; IG, BP 470,079.

While their brilliance of shade and fastness to light render the phthalocyanines valuable for many coloration purposes, they possess other properties which make them specially suitable for certain materials. The reflection spectrum of copper phthalocyanine is the nearest which has so far been found to approach the ideal "minus red" for the trichromatic printing process. Because of their fastness to lime they find use in distempers and water paints to be applied to freshly plastered walls. Their fastness to alkali enables them to be used for coloring viscose in the mass, and special brands of copper phthalocyanine with the requiste dispersibility are marketed (e.g. Monastral Fast Blue BVS paste). Being very stable to heat, the phthalocyanines are useful for coloring thermosetting plastics.

Miscellaneous Derivatives of the Phthalocyanines

Sulfonic acids. When copper phthalocyanine is treated with 8 times its weight of 26% oleum, first at about 45° and then at 60–61° for 12 hours, a disulfonic acid is obtained. The product can be isolated in a yield of 91.5% by adding the sulfonation mixture to salt solution. The disodium salt is marketed by IG as Sirius Light Turquoise Blue GL and Heliogen Blue SBL.[38] Like other members of the Sirius class, Sirius Light Turquoise Blue GL is a direct cotton dye with high light fastness.

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[74] du Pont, USP 2,334,812.

[75] Jaffe, BeP 450,360–1.

[76] du Pont, USP 2,291,452.

[77] Harmon Color Works, USP 2,327,472.

[77a] American Cyanamid, USP 2,505,744.

Durazol Fast Blue 8GS is a sulfonated copper phthalocyanine which gives brilliant greenish blue shades of excellent fastness to light on cotton, viscose and silk.[78] Being a direct cotton dye the fastness to washing is not good, but it can be somewhat improved by aftertreatment with reagents such as Fixanol. Another copper phthalocyanine containing sulfonic groups is Durazol Fast Paper Blue 10GS (ICI), which is useful for dyeing and surface coloring of paper. By fusion of 4-sulfophthalic acid with copper salts and urea, a bright water-soluble phthalocyanine blue is obtained, which is converted into a green dye by chlorination. The process has had no application because of the high cost.[38] Copper tetra-4-sulfophthalocyanine, prepared from 4-sulfophthalic acid, is redder in shade than the product of the direct sulfonation of copper phthalocyanine; the greenness of the latter indicates the entry of one or more of the sulfonic groups in the 3-position.[78a] Sulfonation of the phthalocyanine from 3,3′,4,4′-tetracyanobenzophenone gives a product which dyes cotton in pale green tints.[78b] When halogenated phthalocyanines are condensed with thiophenols and the products are sulfonated, brilliant light-fast bluish to yellowish green dyes for cellulose fibers are obtained.[78c]

Monosol Fast Blue 2GS (ICI) is a sulfonated copper phthalocyanine which is used as a soluble lake color, giving the best results as a barium lake. Salts of the sulfonated phthalocyanines with organic bases,[79] or with ammonium, sulfonium or phosphonium bases containing large alkyl groups[80] have also been used. A salt of copper phthalocyanine trisulfonic acid with dimethylpentadecylamine is marketed as Zapon Fast Blue HL (IG).[47] The diarylguanidine (particularly di-*o*-tolylguanidine) salts of carboxylic acids and sulfonic acids of metal-free phthalocyanines are spirit-soluble, and color cellulose nitrate lacquers in fast shades.[81]

Sulfonamides. By the action of chlorosulfonic acid (9 parts) on copper phthalocyanine at 30°, a tetrasulfochloride can be obtained.[82]

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[78] IG, BP 457,796. The sulfonic acids of phthalocyanines derived from diphenyl have improved substantivity; IG, BP 470,542; 491,151.

[78a] See also Linstead and Weiss, *JCS* 2975 (**1950**).

[78b] Ciba, USP 2,492,732.

[78c] Gutzwiller and Sandoz, USP 2,465,089.

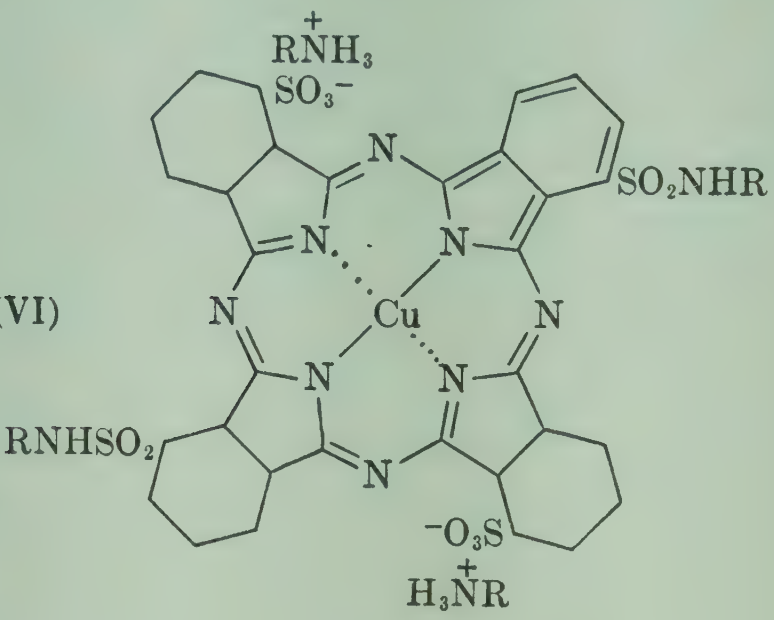
[79] IG, BP 460,147.

[80] ICI, FP 807,052.

[81] Carleton, Woodward and du Pont, USP 2,153,740.

[82] IG, BP 515,637.

Partial hydrolysis with water converts one or two of the sulfonyl chloride groups into sulfonic groups, and when the product is treated with isohexylamine and caustic soda, a mixed sulfonamide-ammonium sulfonate, such as (VI; R = $EtCH_2—CHMe—CH_2NH_2$ is obtained. This is marketed by IG as a lacquer color, Zapon Fast Blue HFL.[83] Zapon Fast Blue FLT was a similar product using *iso*undecylamine.[47]



(VI)

The tetrasulfonamide of copper phthalocyanine made from 4-sulfonamidophthalic acid is stated to be a useful direct cotton dye.[47]

The hydrazides formed by heating a phthalocyanine sulfonyl chloride with hydrazine or an arylhydrazine are alkali-soluble and are substantive to cotton, wool and silk. They are also suitable for writing ink fluids, being rendered quick drying by a small amount of caustic alkali.[84] Similar dyes can be prepared by using polyhydroxyalkylamines or aminopyridines.[84] A chrome-printing dye is obtained by the condensation of 5-aminosalicylic acid with a copper phthalocyanine sulfonylchloride,[83] and the dye would probably have been made by IG commercially in normal times.[38]

Carboxylic acids. The phthalocyanines can be carboxylated by the action of trichloroacetic acid,[85] and by the action of phosgene and aluminum chloride;[86] in the second method the acid chlorides are the initial products.

A tetraphenylphthalocyanine tetracarboxylic acid is the direct cotton dye, Sirius Light (or Supra) Green FFGL, which was developed by IG shortly before the war.[38, 49] The route (Chart 1) was through the Diels-Alder reaction between cinnamic acid and dimethylbutadiene, dehydrogenation and oxidation of the adduct to form (VII), and the phthalocyanine reaction on (VII).

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[83] IG, DRP 696,591. Cf. IG, BP 520,199.

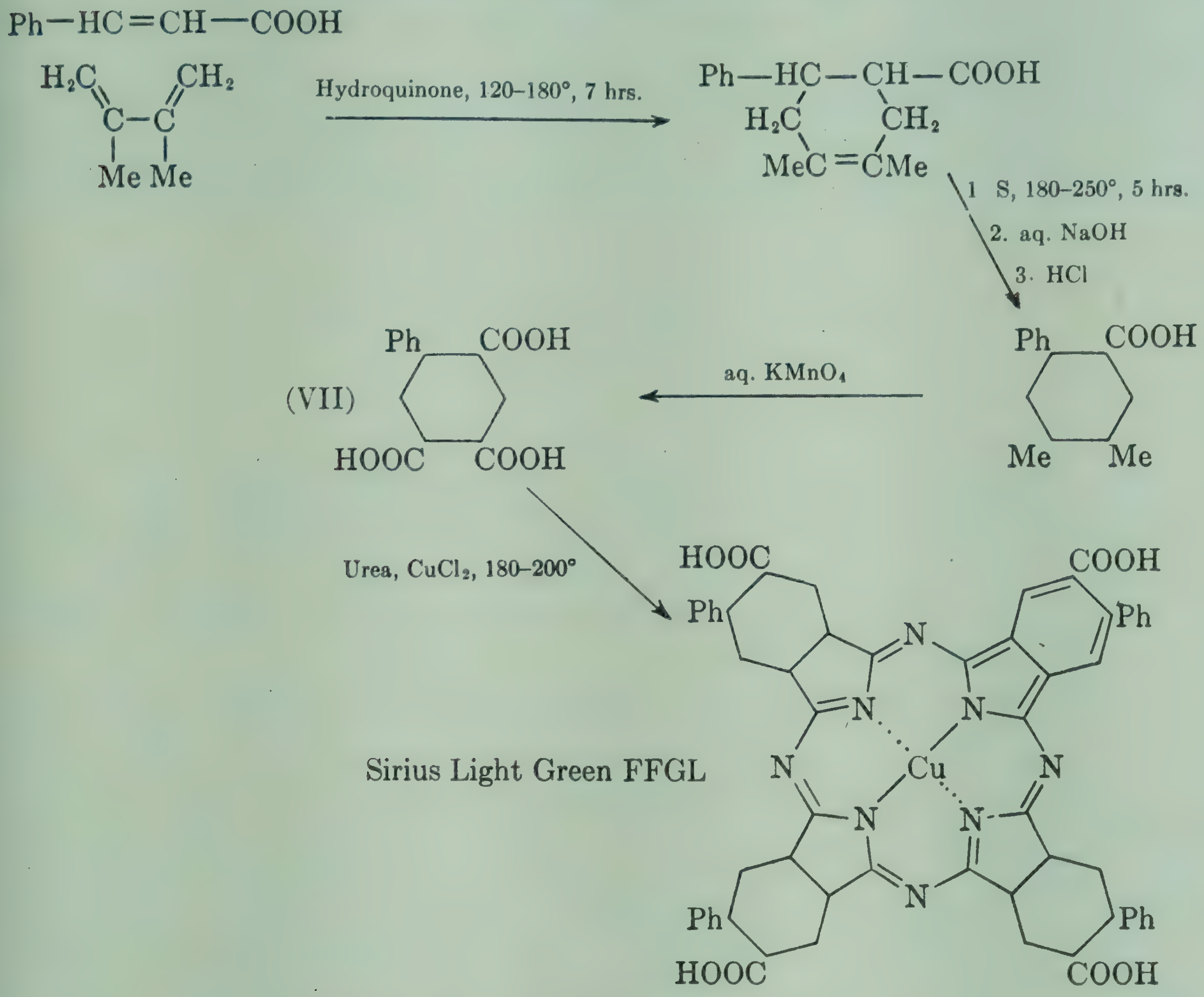
[84] General Aniline and Film, USP 2,413,224; see also BP 613,781–2; 614,407.

[85] IG, BP 487,261.

[86] IG, BP 510,901.

CHART 1

PREPARATION OF SIRIUS LIGHT GREEN FFGL


Ph—HC=CH—COOH
H₂C CH₂ C—C Me Me
Hydroquinone, 120–180°, 7 hrs.
Ph—HC—CH—COOH H₂C CH₂ MeC=CMe
1 S, 180–250°, 5 hrs.
2. aq. NaOH
3. HCl
Ph COOH Me Me
aq. KMnO₄
(VII)
Ph COOH HOOC COOH
Urea, CuCl₂, 180–200°
Sirius Light Green FFGL
HOOC Ph COOH Ph N N N Cu N N N N N Ph HOOC Ph COOH

Nitro- and aminophthalocyanines. By the action of urea and copper on aminophthalimide and of copper on aminophthalonitrile, phthalocyanines are obtained which do not contain primary amino groups. As stated earlier, the phthalocyanines cannot be nitrated, and nitrophthalocyanines have to be prepared from nitrophthalic acid and its derivatives. The nitrophthalocyanines can be reduced to the amines by sodium sulfide;[87] the amines can also be prepared by hydrolysis of the acetamidophthalocyanines with sulfuric acid.[40, 88] The amino groups are diazotizable, and the diazonium salts dye cotton directly. When the dyeings are developed with azoic coupling components, or treated with reagents which decompose the diazonium groups, fast violet, green, and gray shades are produced;[89] but there are practical difficulties in diazotization and coupling, and the shades are not particularly attractive, so that these patents have not been exploited. The diazonium salts offer as usual a convenient route for the synthesis of other derivatives, such as the thiocyano and mercapto compounds.[90] Tetrapyridylphthalocyanines can be prepared by the reaction of tetra-diazotized tetraaminophthalocyanines and pyridine.[91]

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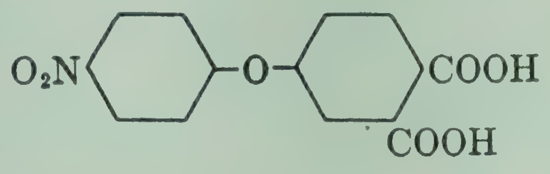
[87] Haddock and ICI, BP 529,847.

[88] IG, FP 809,785.

[89] Blackshaw, Haddock and ICI, BP 535,935.

Phthalocyanines containing an aminophenyl group, attached to each benzene ring by oxygen, or a carbonyl or sulfone group, are prepared by starting with the corresponding phthalic acid derivative, e.g. (VIII), and



(VIII)

finally reducing the nitro groups. These amino groups are readily diazotizable, and azo dyes can be produced by coupling with suitable components.[92] The diazonium salts are more stable than those prepared from the amines in which the amino groups are directly attached to the phthalocyanine nucleus.

Quaternary ammonium and ternary sulfonium salts. Basic dyes, which yield light-fast shades on tannin-mordanted cotton, are obtained by converting copper tetraminophthalocyanine into a quaternary ammonium chloride, or by the introduction of quaternary ammonium groups in other ways. Thus, refluxing the *N*-octachloroacetyl derivative of copper tetraminophthalocyanine with pyridine gives the water-soluble copper octapyridinoacetyl tetraminophthalocyanine octachloride, which dyes tannin-mordanted cotton a bright yellow-green, fast to light and washing.[93]

The tetrapyridylphthalocyanines[91, 94] provide a method of solubilizing phthalocyanine pigments; when converted into pyridinium salts by normal methods, they give water-soluble dyes for cotton and viscose, blue-green to green in shade and fast to washing and light.[95] Other quaternary ammonium and ternary sulfonium salts, which have the remarkable property of dyeing cellulose fibers directly, have been described. Alkyl- or aralkylthiolphthalocyanines can be prepared from

[90] Haddock and ICI, BP 541,146.

[91] Haddock and ICI, BP 530,881.

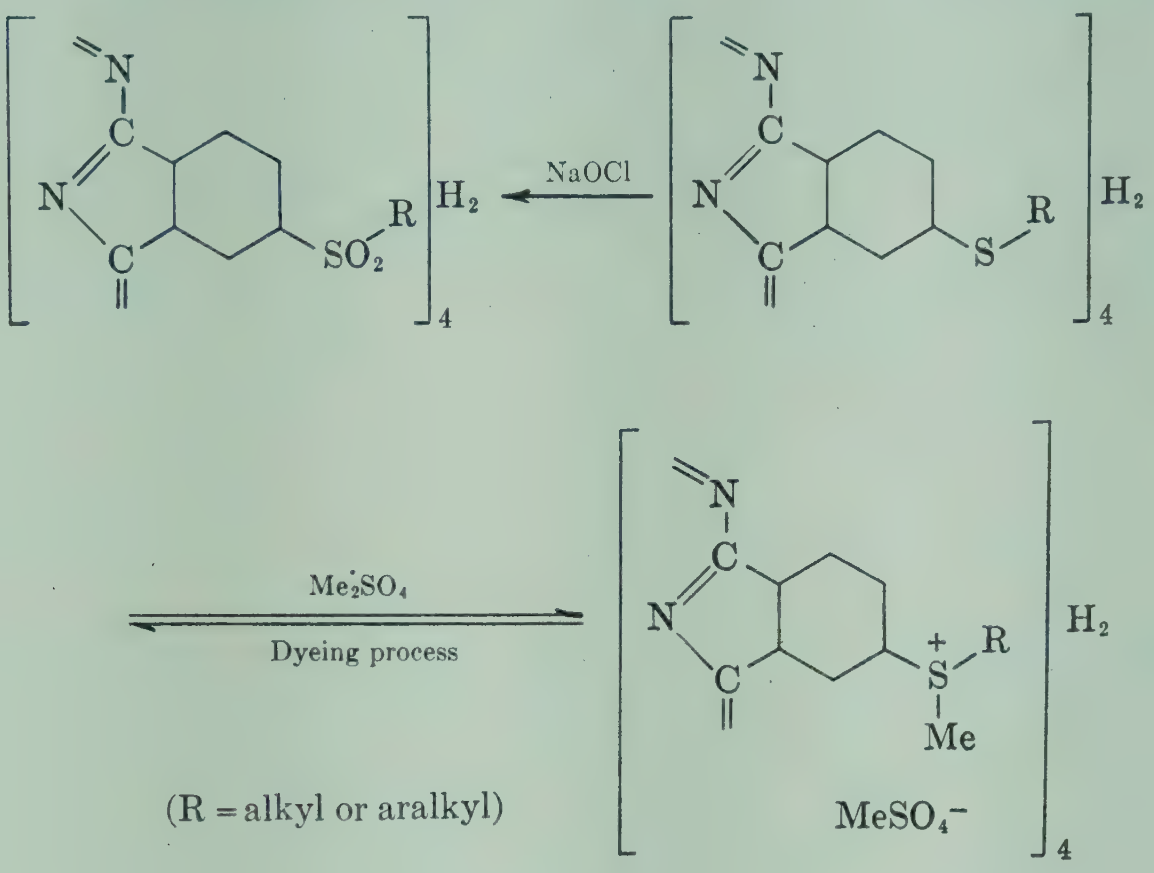
[92] Haddock, Parkinson *et al.* and ICI, BP 569,200; 589,118; 603,753; USP 2,414,374; 2,430,052; 2,479,491.

[93] Linch and du Pont, USP 2,414,050.

[94] Bradbrook *et al.* and ICI, USP 2,277,629.

[95] Bradbrook, Coffey, Haddock, and ICI, BP 522,293; USP 2,277,628.

o-dihalogenophenyl alkyl sulfides and cuprous cyanide or from alkyl- or aralkyl-thiophthalic acids, urea, and a metal compound; the soluble sulfonium salts obtained by heating with an alkyl sulfate or sulfite dye vegetable fibers in bright green shades, converted into fast greenish blues by hypochlorite.[96, 97] One of the drawbacks in these methods of solubilization is that the brilliant turquoise blue of copper phthalocyanine changes to less attractive shades. When the solubilizing groups are linked to the phthalocyanine molecule by a methylene bridge, the bright blue of the original pigment is retained. By treating a solution of copper phthalocyanine in a flux of aluminum chloride and triethylamine with bischloromethyl ether, two or more chloromethyl groups can be introduced.[98] Copper tetrachloromethylphthalocyanine heated with sodium methyl sulfide in alcoholic solution gives the corresponding methylmercaptomethylphthalocyanine; the ternary sulfonium salt obtained by heating this compound with dimethyl sulfate is a bright blue direct cotton dye.[99] Alternatively, chloromethylated copper phthalocyanine may be directly converted into a pyridinium salt or a tetraalkylthiuronium (or isothiuronium) salt by heating with pyridine



(R = alkyl or aralkyl)

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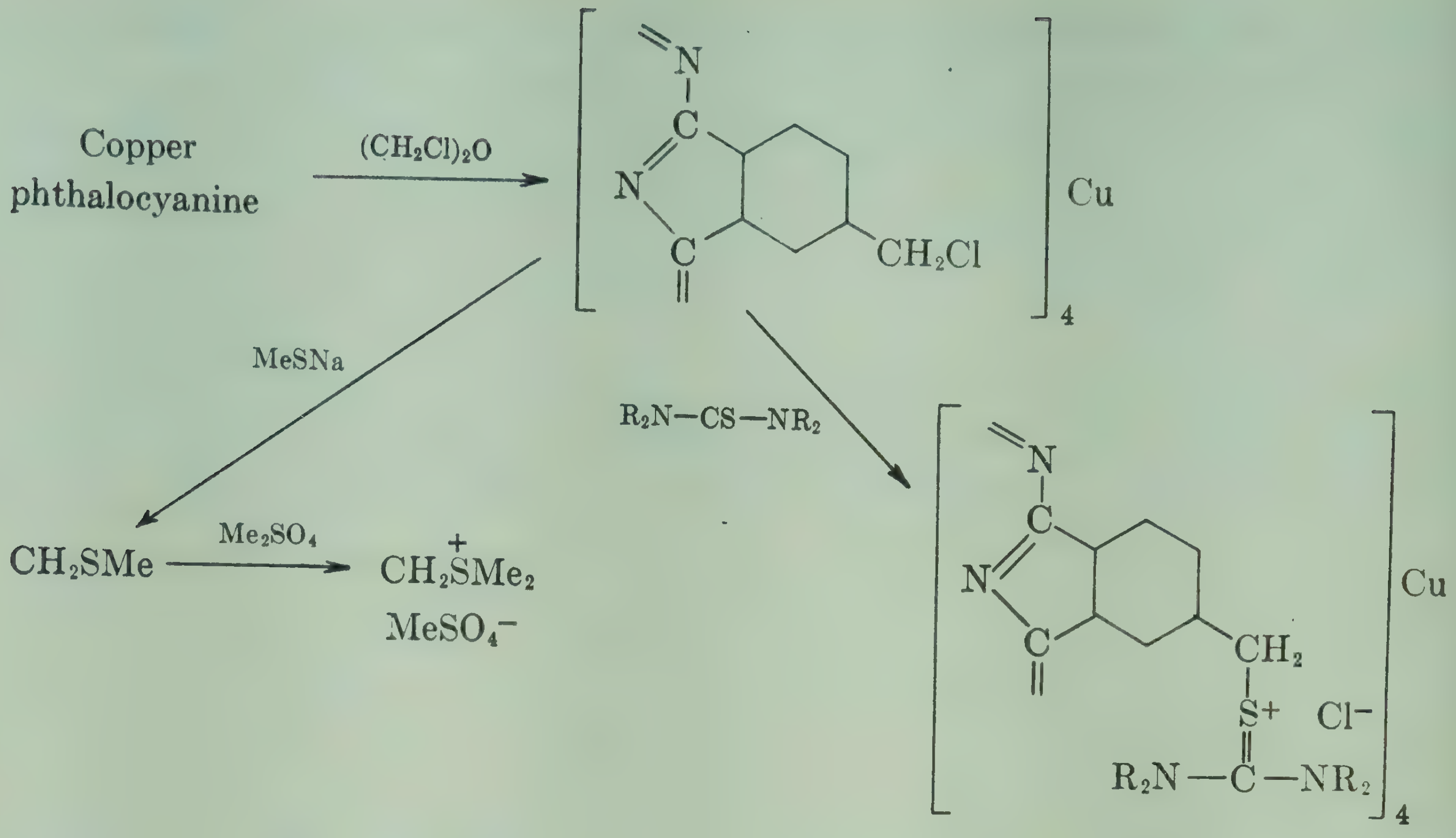
[96] Coffey, Haddock, Jackson and ICI, BP 525,237.

[97] Haddock, *Research* **1,** 685 (1948); Haddock, Wood and ICI, BP 576,270; 587,636; 619,035; 639,487; USP 2,464,806; 2,482,172.

[98] Haddock, Wood and ICI, BP 586,340; USP 2,435,307.

[99] Haddock, Wood and ICI, BP 587,636.



or a tetraalkylthiourea.[97, 99a, 99b] Alcian Blue 8G, an important ICI discovery, is a product of this type derived from Monastral Fast Blue B, which is of great value in calico printing. The beautiful turquoise shade has good all-round fastness properties. The dye is water-soluble, but is rendered insoluble by normal printing methods. The general method of application in printing is to make a paste of an aqueous solution of the dye, an organic acid (e.g., acetic or lactic acid), sodium acetate and starch or starch-tragacanth thickening. After printing and drying at 100–110°, fixation is completed by steaming for a few minutes. The weakly acidic printing mixture becomes weakly alkaline by heating and steaming; the solubilizing component of the dye is thus decomposed and the insoluble pigment is fixed on the fiber.

Sulfur dyes. Treatment of copper phthalocyanine with sulfur monochloride-aluminum chloride complex, which is a new general reaction for the preparation of sulfide dyes (see Chapter XXXV), gives a bright green sulfide dye, applicable as usual from a sodium sulfide bath; Thionol

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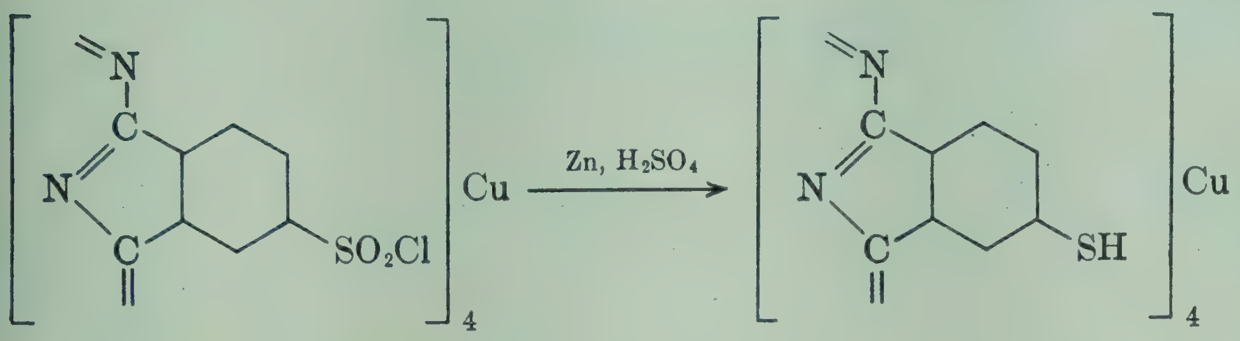
[99a] See also ICI, Chadderton and Thornton, BP 633,160; Butterworth, Vickers and ICI, BP 633,602.

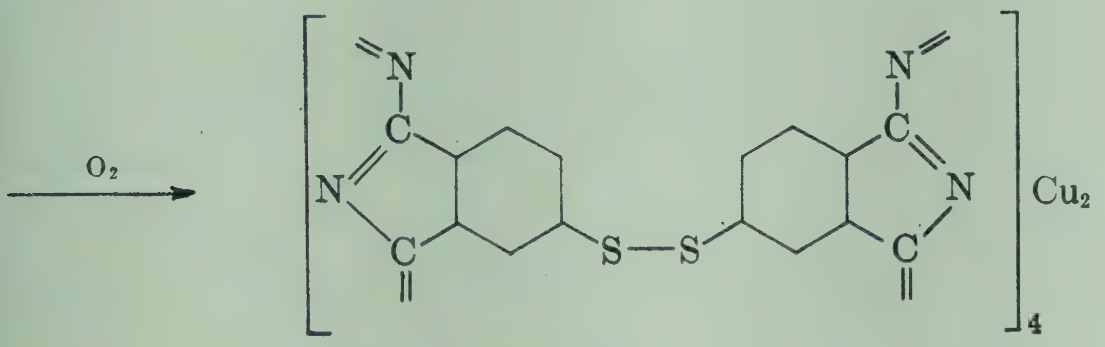
[99b] ICI have applied these reactions for the preparation of water-soluble dyes from anthraquinonoid vat dyes. Acedianthrone, dibenzanthrone, etc., are chloromethylated by treatment with paraformaldehyde or 1,1′-dichloro (or dibromo)-dimethyl ether and aluminum chloride in presence of a tertiary amine not susceptible to halogenomethylation, and then converted into quaternary ammonium salts by treatment with pyridine or triethylamine, or into ternary sulfonium salts by conversion into alkali metal mercaptides and subsequent treatment with dimethyl sulfate or methyl *p*-toluenesulfonate, or into thiuronium salts by means of alkylthioureas (BP 612,222; 613,980–4; 623,997–8).

Ultra Green B, apparently a dye of this type, has light fastness 7 and chlorine fastness 4, the latter being unequalled among the sulfide dyes.

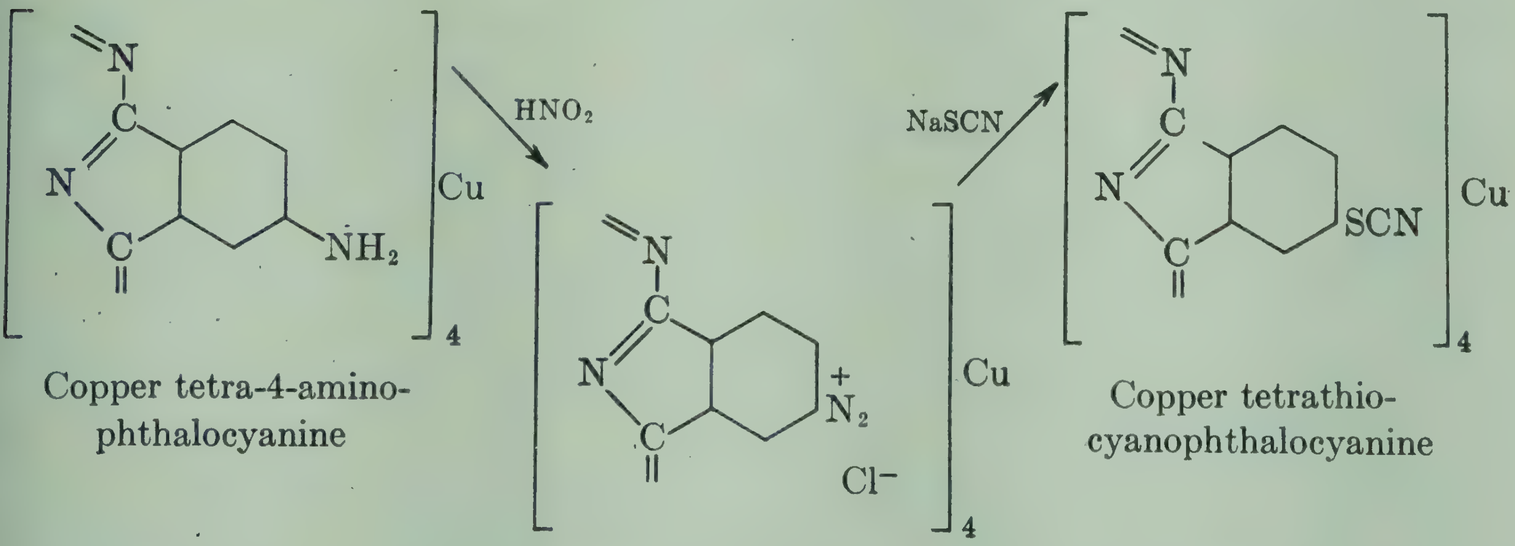
Sulfonyl chlorides are obtained by the action of chlorosulfonic acid on phthalocyanines,[82] and these can be reduced to mercaptans by zinc and acid.[100] The mercaptans and the corresponding disulfides behave as sulfur dyes, giving bright green shades with excellent fastness to light and washing. Sulfur dyes, mainly green in color, are obtained by heating a phthalocyaninesulfonyl chloride with a thiol such as benzylthiol, 2-thiolbenzothiazole, toluene-*p*-thiol, or thioamides,[101] or with phosphorus pentasulfide.[102] Thiocyanophthalocyanines, which may contain 1–4 SCN groups and are prepared from the corresponding diazonium salts, are applicable to cotton from a sodium sulfide bath like the sulfide dyes, and the bright blue-green shades are fast to light and washing.[90, 103]



Copper tetramercapto-phthalocyanine



Insoluble polydisulfide (bright green)



Copper tetra-4-amino-phthalocyanine

Copper tetrathiocyanophthalocyanine

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[100] Haddock and ICI, BP 544,953.

[101] Haddock, Wood and ICI, BP 566,740–1.

[102] Wood and ICI, BP 588,696; USP 2,453,953.

[103] Haddock and ICI, BP 541,146; USP 2,395,117.

Heating copper phthalocyaninetetra-(4)-sulfonyl chloride with thiourea (or a substituted thiourea) or mercaptans, the products are blue to green sulfur dyes.[104]

Vat dyes. Anthraquinone-1-carboxyl chloride condenses with the phthalocyanines to form a vat dye, which gives blue shades on cotton.[105] Vattable phthalocyanines have also been made by building up the phthalocyanine from intermediates containing vattable groups; thus a green vat dye is obtained by treating the 3,4-dichloroanilide of anthraquinone-2-carboxylic acid with cuprous cyanide.[106] However, such vat dyes appear to have little practical value, owing to the danger of hydrolysis of phthalocyanine to phthalimide during vatting. Indanthrene Brilliant Blue 4G (By), which has poor fastness to chlorine, is a derivative of cobalt phthalocyanine. Sulfuric esters of phthalocyanines derived from anthraquinone have been recently described.[107]

Phthalocyanines produced on the fiber. Phthalogen Blue F3G (or IF3G) (By) is a cream-colored water-soluble substance, yielding phthalimide on acidification. Blue and blue-green prints can be produced on cotton by printing a mixture of Phthalogen Blue, Levasol P (a solvent), a copper or nickel salt and ammonium acetate in gum tragacanth thickening, followed by heating at 135–140° for a few minutes or by steaming.

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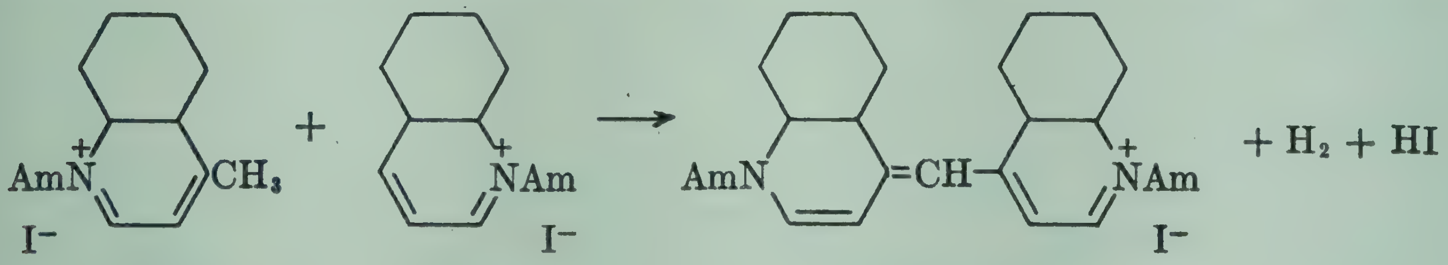
[104] Haddock, Wood and ICI, USP 2,416,386–7.
[105] IG, FP 852,912.
[106] IG, BP 490,017. See also IG, DRP 721,021; FP 852,912; 832,114.
[107] Haddock, ICI *et al.*, BP 633,478.

CHAPTER XXXVIII

CYANINE DYES

The ordinary silver bromide photographic film or plate is sensitive only to violet and blue in the visible region and to ultraviolet light.[1, 1a] Vogel (1873) found that the addition of certain dyes to the photographic emulsion rendered the coated plate sensitive to other parts of the spectrum. Using the red dye coralline (ST 844), which absorbs green, he achieved a weak sensitization for the green part of the spectrum, and among the green aniline dyes, of which some absorbed red strongly, he found one that served as a red sensitizer. A survey of dyes was subsequently undertaken, and it was found that by no means all dyes had the property of behaving as photographic sensitizers. Further, it was slowly realized that for the effect to be observed to the fullest extent, a dye should be exceptionally pure and used in rather high dilution. In the course of time there were found more and more effective *optical* or *color sensitizers*, as they came to be called; and with the discovery of dyes which sensitized a photographic emulsion for the green and red parts of the spectrum, black and white photography, giving a reasonably faithful tone reproduction of colored objects, became possible. Color photography, also, only became realizable in practice after the discovery of efficient sensitizing dyes.

One of the first dyes examined for its photographic effect was cyanine, a dye originally made in 1856 by Greville Williams. The dye was the first of a very large group, known today by the general name of cyanine dyes, and it is among this group that the most powerful and practically



Lepidine isoamyl iodide

Quinoline isoamyl iodide

Cyanine Blue
(λ max. in alc.5920,5540A)

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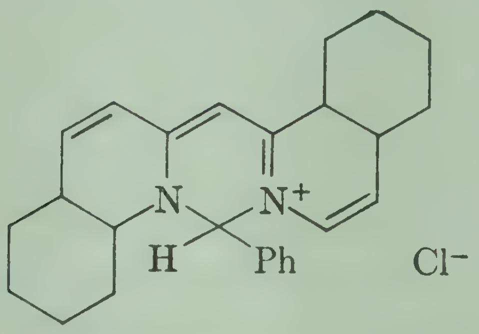
[1] See Mees, The Theory of the Photographic Process, Macmillan, New York, 1942; especially Chapter XXIII on Spectral Sensitivity by Brooker and Carroll; Chapter XXIV on The Sensitizing and Desensitizing Dyes by Brooker; and Chapter XXV on The Mechanism of Optical Sensitizing.

[1a] The cyanine dyes have been recently reviewed by Hamer, *Quart. Revs.* **4**, 327 (1950).

valuable photographic sensitizers have been found. Cyanine or Quinoline Blue (CI 806) was made by Greville Williams by heating the isoamyliodides of (what was later shown to be a mixture of) quinoline and lepidine with caustic alkali, which is typical of a general reaction for the synthesis of the monomethine or simple cyanines. Cyanine is thus one of the oldest synthetic dyes, being contemporaneous with Perkin's Mauve, but the sensitizing properties of Cyanine Blue were only observed many years later by Vogel (1875); the indicated structure of the dye was first suggested by König in 1906. Cyanine Blue sensitizes in the orange-red region (maximum sensitization at 5800–6100A). Quinoline Red (AGFA) (Jacobsen, 1882; CI 805), synthesized by heating benzotrichloride, quinaldine and isoquinoline in presence of a condensing agent, sensitizes to green and yellow. These early cyanines, Cyanine Blue and Quinoline Red, have become obsolete, owing to the bad keeping qualities and the fogging of emulsions prepared from them. Notable advances were then made in the period 1902–1906, when Pinaverdol and Pinachrome, which were sensitizers for the green and orange, and Pinacyanol, which sensitizes throughout the red region, were discovered at Höchst (MLB) (König, Homolka). Commencing with Williams in 1856, Hofmann, Hoogewerff and van Dorp, Miethe, König, O. Fischer, Kaufmann and several other investigators have contributed to our knowledge of dyes of the general type made from quinoline or other heterocyclic nitrogen compounds and alkyl halides. There was extensive activity in this field during the first great war and the years that followed, because of the importance of aerial photography for reconnaissance purposes and the shortage of sensitizing dyes in Great Britain and the United States. The need for red and infrared sensitization when photographs are taken from great heights arises from the atmospheric scattering of light of shorter wave length. Pope, Mills, Hamer and Brooker have been responsible for much of the basic chemical work on the cyanines, and in recent years Brooker has made effective use of the simple and progressive structural variations possible among the cyanines for a quantitative interpretation of color-constitution relationships.[2]



Quinoline Red

Considerable progress has been made in recent years in understanding the mechanism of optical sensitizing.[1] The sensitizing dyes commonly used are of the cyanine or polymethine type, almost the only exception being Erythrosine. Under the conditions employed for sensitizing, the dyes are molecularly dispersed, but aggregation and resultant changes in absorption spectra have been observed at higher concentrations,[2, 2a] and aggregation in the adsorbed state is possible. The relation between degree of sensitizing and molecular aggregation of the dye has been recently investigated by Natanson.[3] A cyanine dye may sensitize in different regions of the spectrum in accordance with the state of aggregation.[4] Leermakers, Carroll and Staud have shown that the sensitizing spectrum (cf. Fig. 2) corresponds precisely to the absorption spectrum of the dyed silver halide, which is about 200–400A nearer the red than the absorption of the dye in aqueous solution.[4] The longer the wave length of sensitization the smaller is the amount of sensitizer required, because of the efficiency of energy transfer from dye to silver halide; the amount of sensitizer usually employed is a few parts per million. Mott has suggested that increased absorption in the sensitized region induced by the dye provides a source of energy which contributes to latent image formation.[5] When silver bromide adsorbs a cyanine dye under conditions in which there is optimum sensitization, the leaf-like dye molecules form an edge-on monomolecular layer, in which the packing is as close as the structure of the dye and the crystal lattice of the silver halide will permit. Planarity is a characteristic of the sensitizing dyes.[1, 5a]

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[2] See Chapter VIII.

An interesting phenomenon in optical sensitizing is supersensitizing by mixtures of dyes, and by compounds which have no sensitizing activity by themselves, of which numerous examples have been mentioned in patents. Thus the sensitivity of a cyanine dye can be doubled or trebled by adding an ammonium or alkali aurous thiocyanate to the emulsion.[5b]

Since the cyanine dyes lack fastness to acids and to light, they are of very limited interest for textiles, but a few members of the series have recently found use as basic dyes, particularly in calico printing, and as cellulose acetate dyes.

[2a] For a study of the fluorescence of cyanine and related dyes in the monomeric state, see Hofer, Grabenstetter and Wiig, *JACS* **72**, 203 (1950).

[3] *Acta Physicochim. U.R.S.S.* **21**, 430, 437, 451 (1946).

[4] *J. Chem. Phys.* **5**, 878; 889; 893 (1937). See also Natanson, *Nature* **140**, 197 (1937).

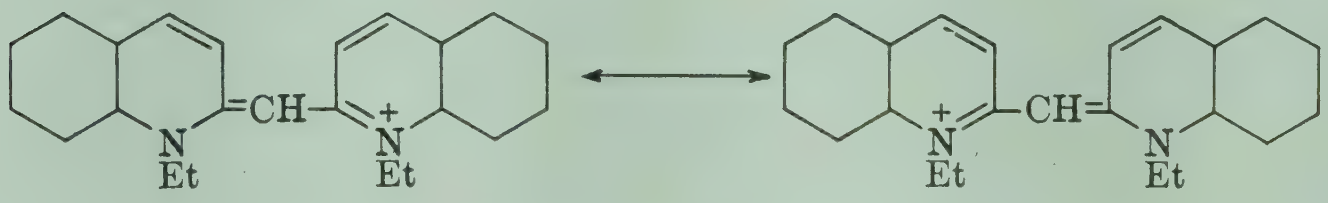
[5] *J. phys. radium* **7**, 249 (1946); see also Simpson, *J. Chem. Phys.* **15**, 414 (1947); Eggert, Meidinger, and Arens, *Helv. Chim. Acta* **31**, 1163 (1948).

[5a] See also Bruylants, van Dormael, and Nys, *Bull. classe sci., acad. roy. Belg.* **34**, 703 (1948).

[5b] Koslowsky and Mueller (1936), *Bibliography of scientific and industrial reports, U.S. Dept. of Commerce*, **8**, 873; P.B. 70,053.

Classification

While the name Cyanine denoted the deep blue color of Williams' dye, the cyanine dyes now cover nearly the whole of the color range; but they belong to a relatively compact group, considering that many hundreds have been synthesized. The typical cyanine molecule may be defined as being built up of two nitrogen-containing ring systems in one of which the nitrogen atom is tervalent and in the other it is tetracovalent; the two nitrogen atoms are linked by a conjugated chain of an uneven number of carbon atoms. The cyanines are therefore part of the larger group of polymethine dyes, other examples of which are discussed later in this Chapter. In the older dyes, both the halves were derived from quinoline; but pyridine, indole, benzothiazole, benzoselenazole and other heterocyclic derivatives are also known, of which many have found practical application. The two ring systems may be directly united by a bond between nuclear carbon atoms, or the union may be effected by means of a –CH= group or –CH=CH–CH= group or a longer conjugated chain containing an uneven number of carbon atoms. The Neocyanines are exceptional in that they contain three heterocyclic residues, but otherwise they possess all the typical cyanine characteristics. The intense color of the cyanines is associated with a resonance interaction between the nitrogen atoms at the two ends of the conjugate chain, involving the movement of a cationic charge.[2] The cyanine dyes are usually in the form of the iodides, and the anion has therefore not been indicated in formulating most of the cyanine dyes, unless a perchlorate or other salt is specified. A recent patent claims that as sulfamates the cyanine dyes impart greater blue light speed than as iodides.[6]



Since the older cyanines are mainly derived from quinoline, it is convenient to group the quinoline compounds separately and to base further classification of the cyanine dyes on the mode of attachment of the ring systems. Thus the quinoline derivatives fall into four groups, of which the first is very small and unimportant.

I. *Apocyanines:* The ring systems are linked directly by means of nuclear carbon atoms.

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[6] du Pont, BP 566,684.

II. *Cyanines:* (a) *Pseudocyanines;* (b) *Isocyanines;* and (c) *Cyanines:* The ring systems are united by a —CH= group in (a) the 2,2′-; (b) 2,4′-; and (c) 4,4′-positions.

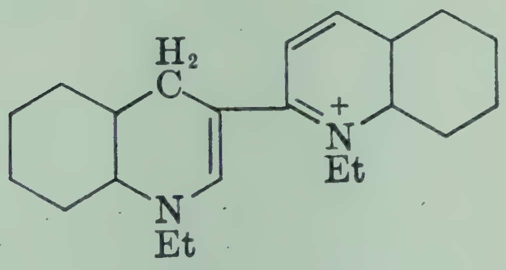
III. *Carbocyanines:* (a) *Pinacyanols;* (b) *Dicyanines;* and (c) *Kryptocyanines:* The ring systems are united by a =CH—CH=CH— group, the difference between (a), (b) and (c) being as in group II.

IV. *Polycarbocyanines:* The ring systems are united by a 5-carbon chain (Dicarbocyanines), 7-carbon chain (Tricarbocyanines), or longer chains.

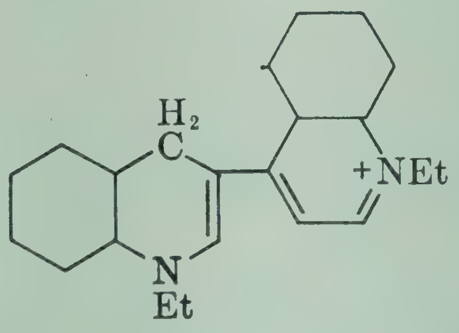
One or both of the quinoline rings in these cyanine types may be replaced by other heterocyclic ring systems, such as indole, benzothiazole and benzoxazole; polymethine dyes may also be prepared in which one or both of the nitrogen atoms at the ends of the polymethine chain are in extranuclear groups.

Apocyanines

When quinoline ethiodide is treated with alcoholic potash, a mixture of two dyes, Xanthoapocyanine (yellow) and Erythroapocyanine (reddish), is obtained, and the constitution of the latter follows from its oxidation to 3,4′-diquinolyl by means of iodine.[7] The apocyanines have no practical interest.



Xanthoapocyanine



Erythroapocyanine

Cyanines

The condensation of 2- or 4-halogenoquinoline methiodide or ethiodide with the reactive 2-methyl group in quinaldine methiodide or ethiodide in presence of alcoholic potash (or preferably triethylamine[8] or an alkali carbonate[9]) gives a pseudocyanine or isocyanine dye.[10] The 2,2′-cyanines or pseudocyanines, which sensitize in the bluish green region of the spectrum, are technically important, while the 2,4′-cyanines or iso-

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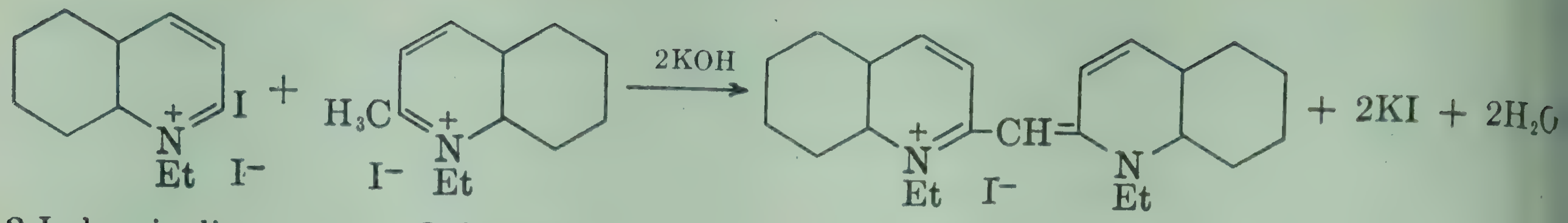
[7] Mills and Ordisch, *JCS* 81 (**1928**).

[8] Brooker and Keyes, *JACS* **57,** 2488 (1935).

[9] Beilenson and Eastman Kodak, BP 435,542.

[10] Hamer, *JCS* 1008 (**1939**); *ibid.*, 206 (**1928**); Fischer, *J. prakt. Chem.* **98,** 204 (1918); Fischer and Scheibe, *ibid.* **100,** 86 (1919).

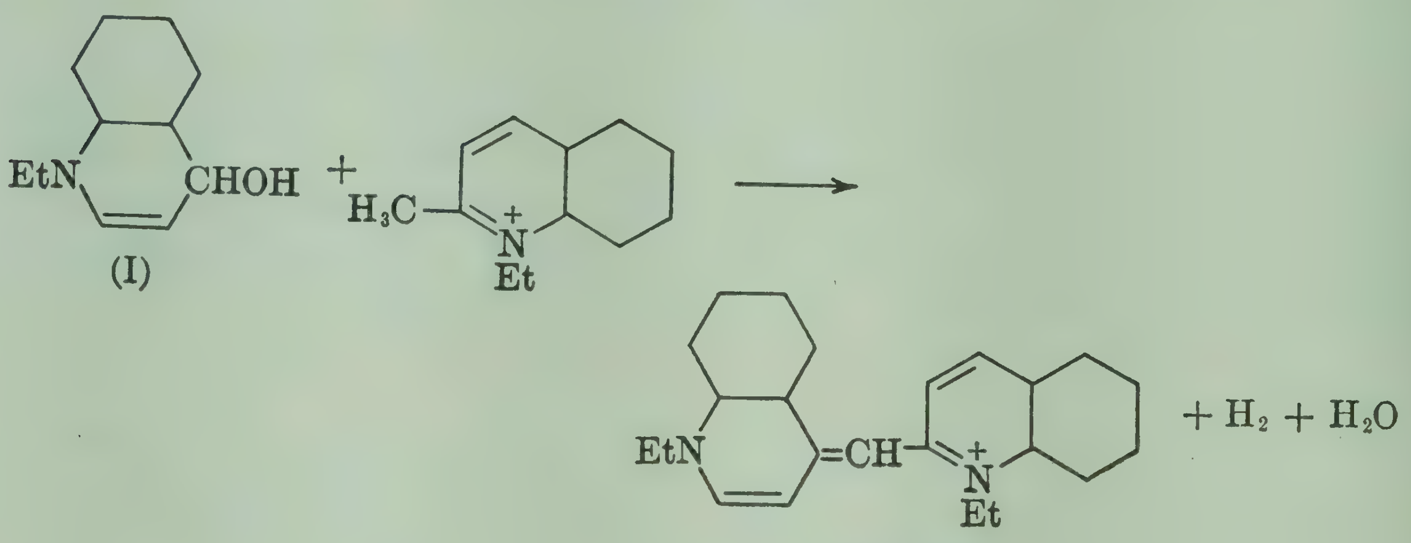


2-Iodoquinoline ethiodide

Quinaldine ethiodide

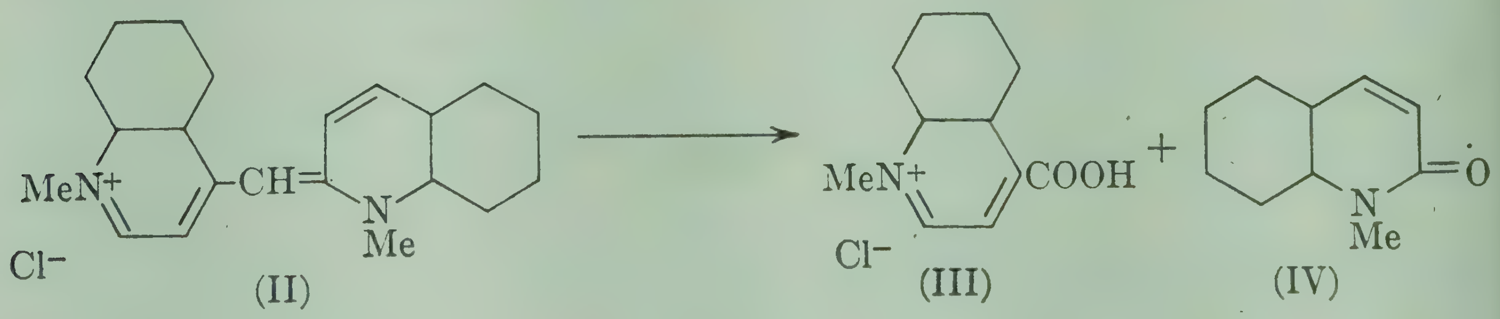
Pseudocyanine

cyanines, once of considerable importance, are no longer in commercial use. Ethyl Red (MLB) (Hoogewerff and van Dorp, 1883; CI 807), made by the interaction of the ethiodides of quinoline and quinaldine, was the first commercial isocyanine; Miethe and Traube discovered its sensitizing action in 1902. Hamer has shown that a yield of 82% can be obtained when quinaldine ethiodide, quinoline ethiodide and caustic alkali are used in molar proportions of 1:3:3.[10] The probable mechanism of the reaction is illustrated for Ethyl Red, and a series of isocyanines have been prepared by this general method. The quinolones do not undergo this condensation; it would appear that (I) reacts with quinaldine ethiodide, and the product then loses two atoms of hydrogen which react with the excess of quinolinium salt that is usually employed.



Ethyl Red

The constitution of the cyanine dyes can be demonstrated by the products of oxidation;[11] thus 1,1′-dimethylisocyanine chloride (II) yields cinchonic acid methochloride (III) and 1-methyl-2-quinolone (IV).



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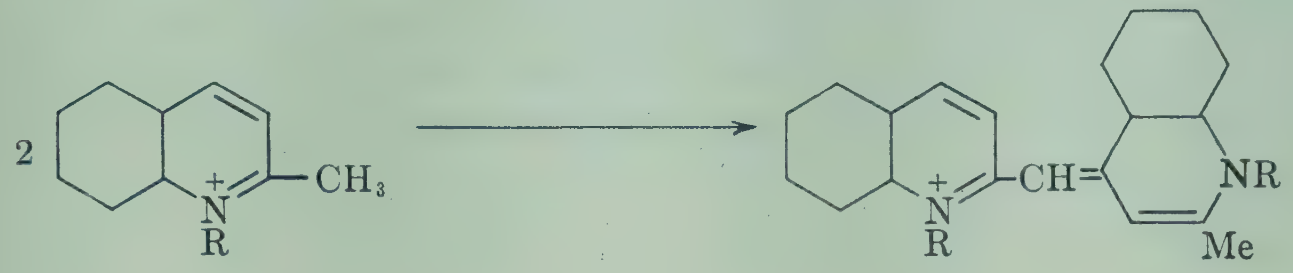
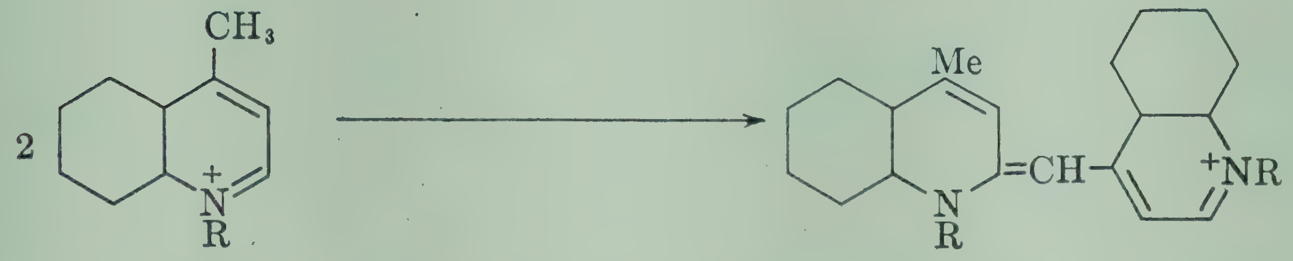
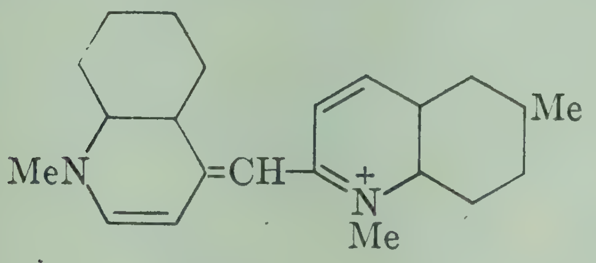
[11] Mills and Wishart, *JCS* **117,** 579 (1920). See also Adams and Haller, *JACS* **42,** 2389 (1920).

Further, a quinaldine alkiodide or a lepidine alkiodide oxidized by itself under certain conditions yields an isocyanine dye, and it is thus clear that a quinaldine molecule must be attached in the 4-position, and a lepidine molecule in the 2-position.

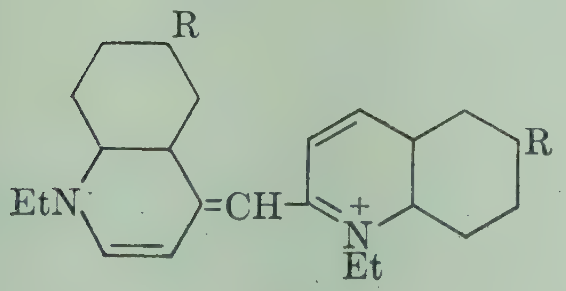




Ethyl Red, which confers max. sensitivity at 5200–5700A, was a better sensitizer than Cyanine Blue, but several isocyanine dyes superior to Ethyl Red were later developed. The main structural variation was the introduction of alkyl, alkoxy and dialkylamino groups in the 6,6′-positions in the isocyanine molecule, and the following are some examples; but these dyes have long been obsolete.



Pinaverdol (MLB; ST Erg. I 923)
Sensitol Green (Ilford)



Pinachrome; R=OEt
Orthochrome T; R=Me
Pinachrome Violet; R=NMe_2

The true or 4,4′-cyanines, exemplified by the earliest cyanine dye, Cyanine or Quinoline Blue, have no technical interest at the present time. They are formed by the reaction mechanism illustrated for Ethyl Red, a lepidine alkiodide being used in place of a quinaldine alkiodide.

CARBOCYANINES[12]

Among the three types of Carbocyanines, the symmetrical compounds, or 2,2′- and 4,4′-derivatives, are of technical importance. If the isocyanine condensation of the alkiodides of quinoline and quinaldine is effected in presence of formaldehyde, blue dyes are formed which have a sensitizing action in the yellow to red region, well beyond the range of the isocyanines (König, 1905). The mechanism of the reaction, which has no technical interest at the present time, is the condensation of formaldehyde with two molecules of the quinaldine component, and the quinolinium salt is not involved (Pope and Mills), although its presence improves the yield (O. Fischer). A general reaction by which the 2,2′-compounds or Pinacyanols and the 4,4′-compounds or Kryptocyanines can be prepared is the condensation of 2- or 4-methylquinoline alkiodide with excess of ethyl orthoformate.[13] König (1922) used acetic anhydride as the condensing agent, but Hamer showed that the reaction proceeds much better in dry pyridine at the boil; the function of pyridine is to absorb the hydriodic acid formed in the reaction, and a yield of over 70% can be obtained.[14] The reaction of quinaldine alkiodide and similar quaternary salts with ethyl orthoformate and other reagents mentioned later is probably preceded by the removal of a proton by the basic catalyst and the formation of the methylene base (I).[15] Hamer's ethyl orthoformate-pyridine method is very useful for the synthesis of symmetrical carbocyanines in general. Symmetrical carbocyanines can also be made by condensing a quaternary salt of a heterocyclic nitrogen compound having a 2- or 4-methyl group with thioformamide, thioformanilide, formamidoxime, or formamide; the last is the least reactive.[15a]

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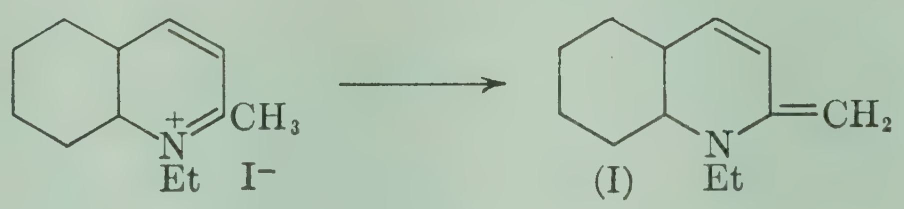
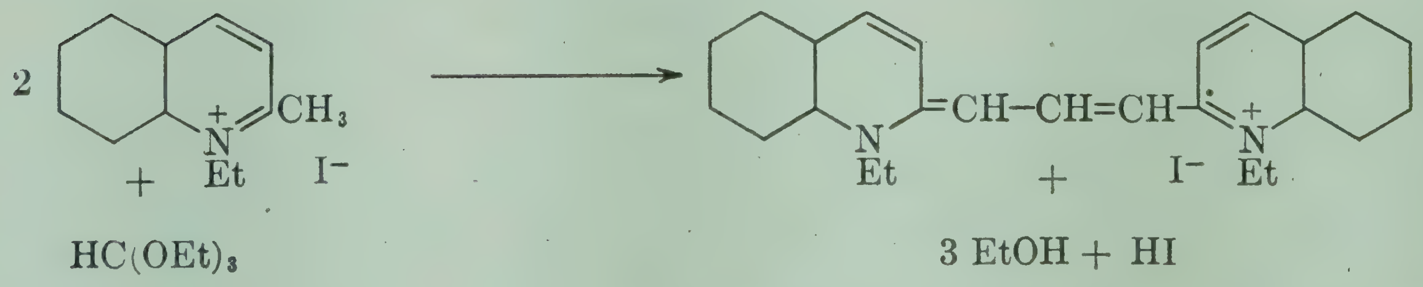
[12] Mills and Hamer, *JCS* **117,** 1550 (1920); Pope and Mills, *Phot. J.* **60,** 253 (1920).

An example of a 2,2′-carbocyanine is Pinacyanol (MLB) (König, 1905; CI 808) (Sensitol Red, Ilford) made from quinaldine ethiodide and





Pinacyanol (blue in alc.solution; λ max. 6040A) ethyl orthoformate; its max. sensitization is in the region 5700–6600A. The constitution of Pinacyanol follows from its formation by the condensation of two molecules of quinaldine ethiodide with one of formaldehyde and from its oxidation with nitric acid to quinaldinic acid ethonitrate.[12] The 6,6′-diethoxy derivative is Pinachrome Blue (ST 924).

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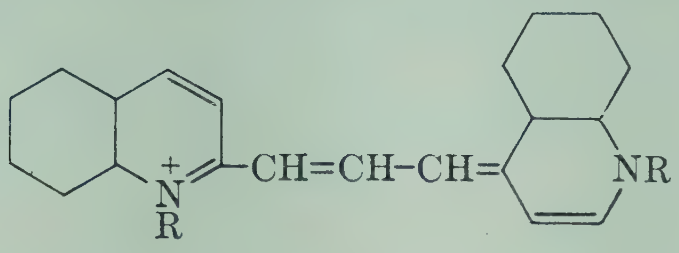
[13] For the preparation of ethyl orthoformate, see Kaufmann and Dreger, *OSCV I*, p. 258.

[14] Hamer, *JCS* 2796 (**1927**); König, *Ber.* **55**, 3293 (1922).

[15] For a discussion of the mechanism of formation of cyanine dyes, see Lal and Petrow, *JCS* S115 (**1949**).

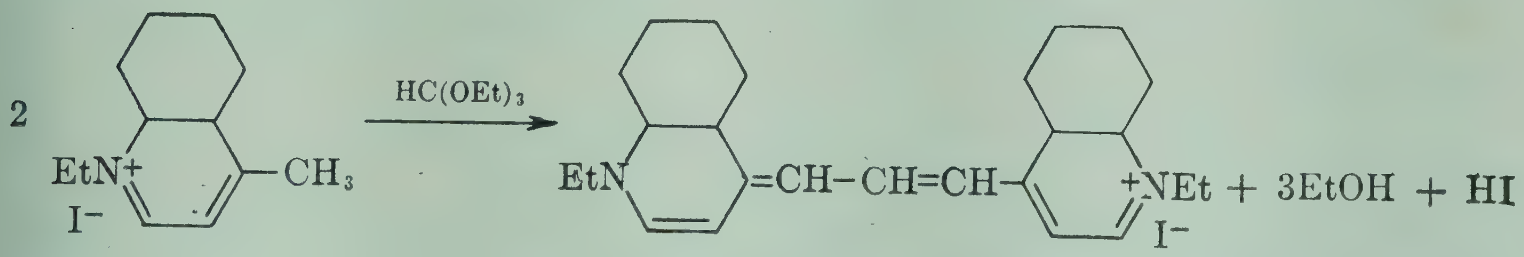
[15a] Knott and Eastman Kodak, USP 2,487,881.

Dicyanines,[16] which are unsymmetrical or 2,4′-carbocyanines, made by MLB in 1906, were useful sensitizers for the infrared until 1919 when the superior Kryptocyanine was discovered. Dicyanine has its maximum sensitizing action at about 6250–7100A. Dicyanines may be prepared


Dicyanine

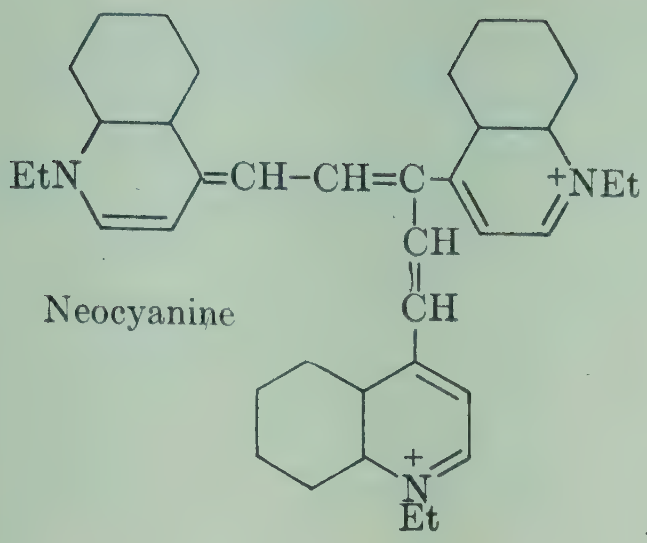
by the interaction of one molecule each of a quinaldinium and a lepidinium salt with ethyl orthoformate.[14]

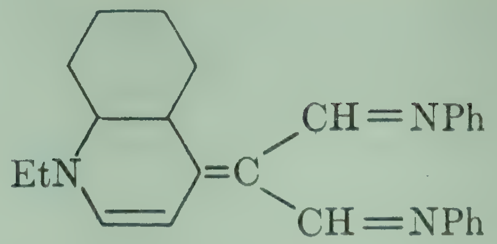
The first 4,4′-carbocyanine to be prepared was Kryptocyanine (Eastman Kodak) (Adams and Haller, 1919; CI 810),[17] which is best made by the action of ethyl orthoformate on lepidine ethiodide in pyridine solution; it is a strong red sensitizer, which has maximum activity at about 7500A and has been useful for sensitizing in the near infrared; but it is no longer used.

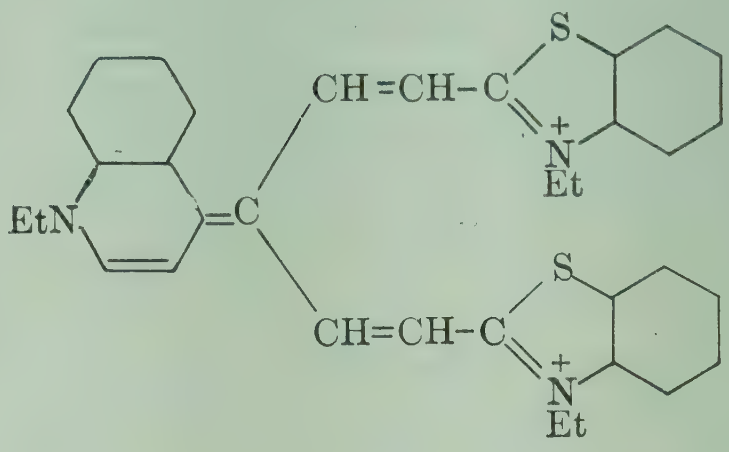

Kryptocyanine (alc. solution greenish blue; λ max. 7050A)

Neocyanine (Eastman Kodak) (Clarke, 1925) may be regarded as a derivative of Kryptocyanine, and was in fact isolated as a less soluble by-product in the preparation of the latter.[1] The correct constitution of Neocyanine was suggested by König[18] and substantiated by Kendall and Majer and by Hamer.[19, 20] For some years it was the best far-infrared sensitizer available (with maximum sensitization at about 8200A), but has now been superseded by the tri-, tetra- and penta-carbocyanines.

[16] Mills and Odams, *JCS* 1916 (**1924**).
[17] *JACS* **42,** 2661 (1920).
[18] König, *Z. wiss. Phot.* **34,** 15 (1935).
[19] Kendall and Majer, *JCS* 690 (**1948**). See also BP 638,023–4.
[20] Hamer, Rathbone, and Winton, *JCS*, 954; 1434 (**1947**).


Neocyanine


(II)


(III)

Neocyanine has been synthesized by condensing the dianilo-base (II) with two moles of lepidine ethiodide in presence of acetic anhydride and sodium acetate.[20] This new synthetical method for preparing neocyanine has been shown to have wide scope, and neocyanines with dissimilar nuclei (e.g. III) have thus been prepared.[21] Kendall and Majer[19] have condensed carbocyanines with heterocyclic quaternary salts containing reactive methyl groups and ethyl trithio-orthoformate[22] in acetic anhydride solution to yield trinuclear dyes of the neocyanine type; they have made the interesting observation that the main product is only one neocyanine although an unsymmetrical carbocyanine is employed.

POLYCARBOCYANINES

Although Kryptocyanine was an excellent infrared sensitizer, there was an intensive search in the years preceding the last war for better and more powerful sensitizers. The cyanines in which the number of carbon atoms between the ring systems is 5, 7 or a larger uneven number may be termed polycarbocyanines, being vinylene homologs of the carbocyanines in which the intervening chain contains 3 carbon atoms. If Q and Q′ represent the two quinoline nuclei, $Q{=}CH(-CH{=}CH)_n-Q'$ represents a polycarbocyanine series; in a dicarbocyanine $n = 2$; in a tricarbocyanine, $n = 3$; in a tetracarbocyanine $n = 4$; and so on. When the length of the carbon chain in a cyanine dye is increased, the absorption shifts to longer wave lengths with the addition of each vinylene group.[2, 23] The limitation to a progressive lengthening of the chain is the difficulty in preparation and the instability of the tetracarbocyanines and the still higher homologs. The shifting of the sensitizing maximum to longer wave lengths can be effected not only by increasing the number of –CH= units in the polymethine chain, but also (and sometimes in a more striking manner) by substitution in the heterocyclic end nuclei. The quinoline polycarbocyanines are less important than other heterocyclic derivatives, especially derivatives of benzothiazole which give rise to thiacarbo- and thiapolycarbocyanines. Some of the methods by which such homologous series may be synthesized are therefore mentioned in the next section in connection with the thiacarbocyanines.

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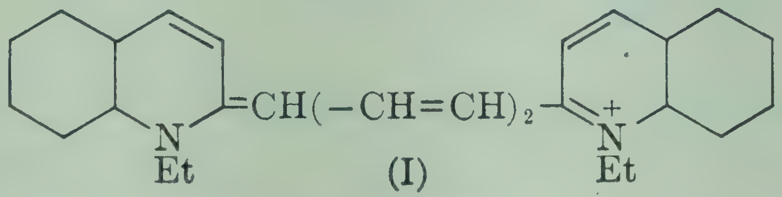
[21] Hamer, Rathbone, and Winton, *JCS* 1872 (**1948**); 1113 (**1949**).

[22] Holmberg, *Ber.* **40,** 1740 (1907).

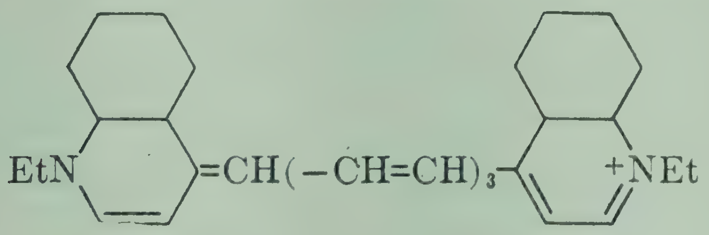
[23] Fisher and Hamer, *Proc. Roy. Soc. London,* **154A,** 703 (1936).

The dicarbocyanine (I) has its sensitizing action at about the same wave length as Kryptocyanine (7500A).[24]



(I)

Tricarbocyanines (1931–35) are infrared sensitizers, whose response goes well beyond 11000A, and an important representative of this group is Xenocyanine, which has maximum activity at about 8500A and which has made the spectral region between 9000 and 11000A readily accessible.[25, 26] Xenocyanine is prepared by an application of a general method for the synthesis of tricarbocyanines which consists in treating a heterocyclic compound carrying a reactive methyl group with glutaconaldehyde dianil hydrochloride (II) in the presence of alcoholic alkali, piperidine or triethylamine.[25, 27] In the preparation of Xenocyanine, (II) is condensed with two moles of lepidine ethiodide. The intermediate (II) is obtained by the interaction of 2,4-dinitrophenylpyridinium chloride with aniline



Xenocyanine

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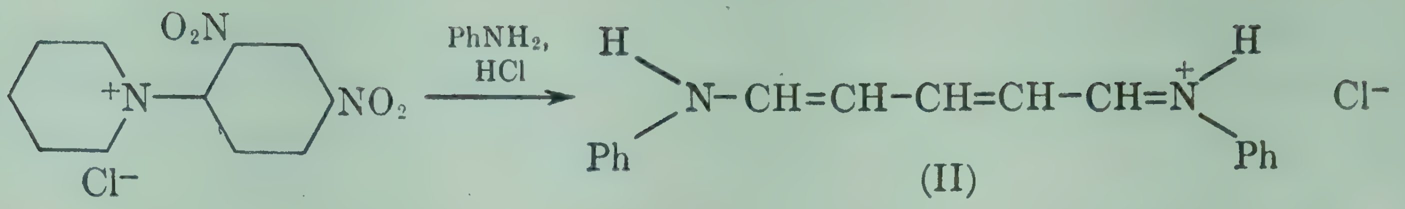
[24] Beattie, Heilbron and Irving, *JCS* 260 (**1932**).

[25] Fisher and Hamer, *JCS* 189 (**1933**).

[26] Clark, *Photography by Infrared*, 2nd Ed., Wiley, New York, 1946; Brooker, Hamer and Mees, *Phot. J.* **73,** 258 (1933); Dieterle, Dürr and Zeh, *Z. wiss. Phot.* **32,** 145 (1933); Meggers and Kiers, *Bur. Standards J. Research,* **9,** 309 (1932).

[27] Brooker, USP 2,095,856; 2,161,332; 2,165,337; 2,189,599; Wahl and IG, USP 1,878,557; DRP 499,967. See also IG, BP 438,449–50; 438,484; Keyes and Eastman Kodak, USP 2,251,286.


(II)

and aniline hydrochloride. The *N*,*N*-dimethyl derivative of (II), obtained from monomethylaniline, can also be used.[28]

Dyes of the tetra- and pentacarbocyanine series, including those containing the chains =CH—CH=CH—CH=C(OAc)—CH=CH—CH=CH— and =CH—CH=CH—CH=C(OAc)—CH=CH—CH=CH—CH=CH— have been prepared, and they sensitize far into the infrared, although they are unstable and photographic plates sensitized by them have poor keeping qualities.[29, 30] Tetra- and pentathiacarbocyanines (see later) are of practical value for infrared sensitization.

Derivatives of Bases other than Quinoline

Numerous cyanine dyes have been prepared in which quinoline is replaced by other nitrogen-containing heterocyclic systems, such as (I) thiazoline, (II) benzoxazole, (III) benzothiazole, (IV) benzoselenazole, (V) and (VI) α- and β-naphthothiazole. The synthetic reactions outlined for the cyanines derived from quinaldine or lepidine are in general applicable to other heterocyclic quaternary ammonium salts having a 2- or 4-methyl group. Thus 2-methylbenzothiazole can replace quinaldine in the reactions for the preparation of Ethyl Red and of Pinacyanol; but the nuclear iodine in 2-iodobenzothiazole alkiodide is not reactive in the condensation[8, 9, 10] used for the synthesis of pseudocyanines and isocyanines. Because of the importance of the cyanines derived from various heterocyclic intermediates, reactions for the synthesis of such cyanines have been extensively studied.

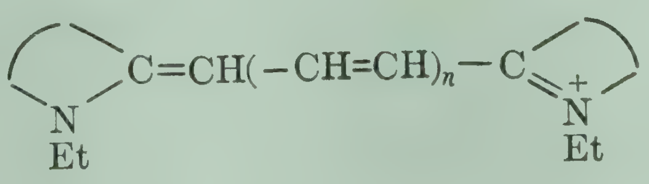

(IX)

Fig. 1 gives the wave lengths of maximum absorption of eight series of symmetrical cyanines (IX), in which $n = 0, 1, 2$ or 3, and the heterocyclic rings are (I)–(VI) listed above, (VII) is 2-quinoline and (VIII) is 4-quinoline. It is clear from Fig. 1 that these heterocyclic nuclei have an increasingly bathochromic effect in the order named.[2] While many technically useful dyes are symmetrically constituted, many cyanines have also been prepared in which the two heterocyclic components are different, as well as types in which only one component is heterocyclic; the unsymmetrical dyes of commercial importance are in fact more numerous.

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[28] Zincke and Würker, *Ann.* **338,** 107 (1905).

[29] Brooker and Keyes, *J. Franklin Inst.* **219,** 255 (1935); Dieterle and Zeh, *Z. wiss. Phot.* **34,** 245 (1935); König, *J. prakt. Chem.* (2) **88,** 193 (1913). See IG, BP 441,624 for the synthesis of polymethine dyes substituted in the polymethine chain of at least 7C atoms by an aryloxy or alkoxy group.

[30] *Z. wiss. Phot.* **36,** 68; 141 (1937); IG, BP 485,623–4; 503,337; 512,470.

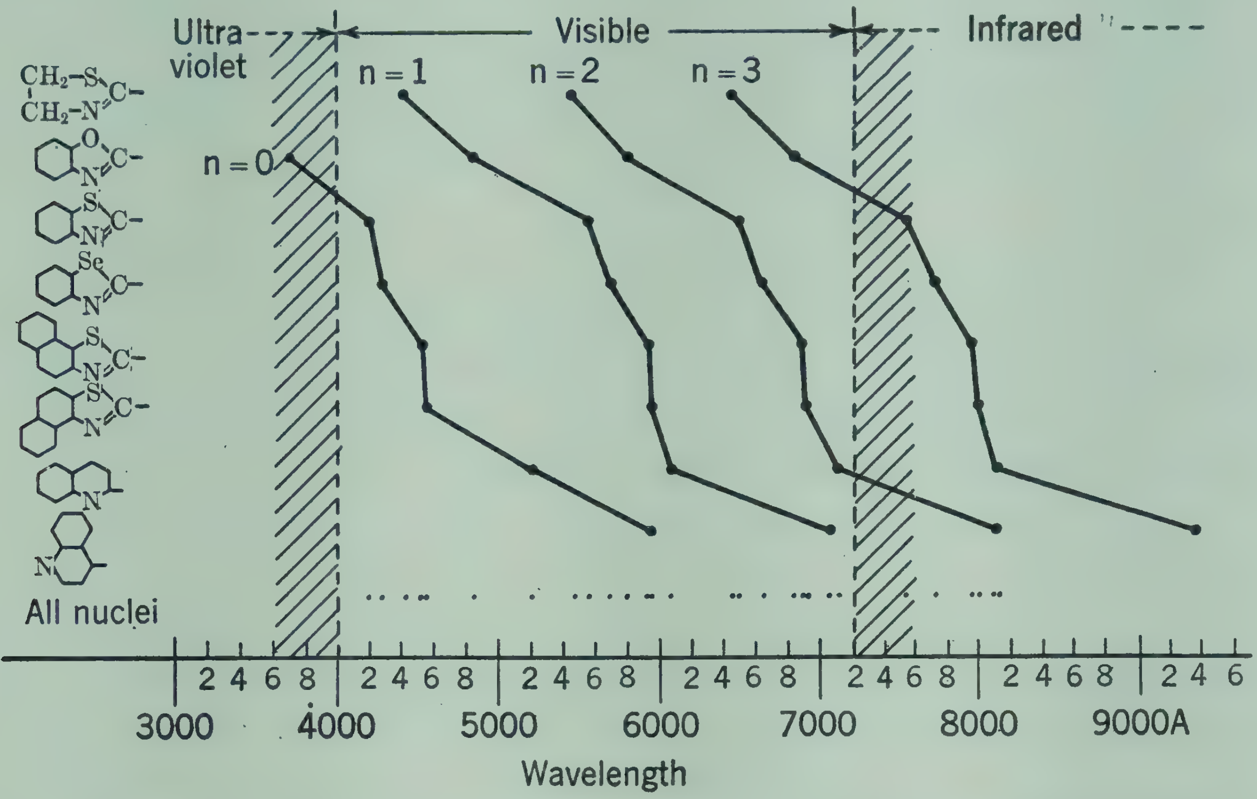
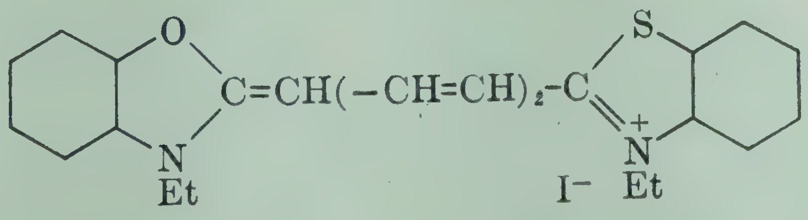


Fig. 1. Wave lengths of maximum absorption in methanol solution of eight vinylene-homologous series of cyanines (Brooker).

Nomenclature. Cyanines derived from various heterocyclic nuclei may be named in accordance with the classification of the cyanines derived from quinoline, given earlier; the other heterocyclic nuclei are indicated by certain conventional prefixes, such as thia- for benzothiazole, oxa- for benzoxazole, and selena- for benzoselenazole. Examples are cited later. In the more systematic Beilstein nomenclature, the usual names of the heterocyclic nuclei, the positions of the substituents

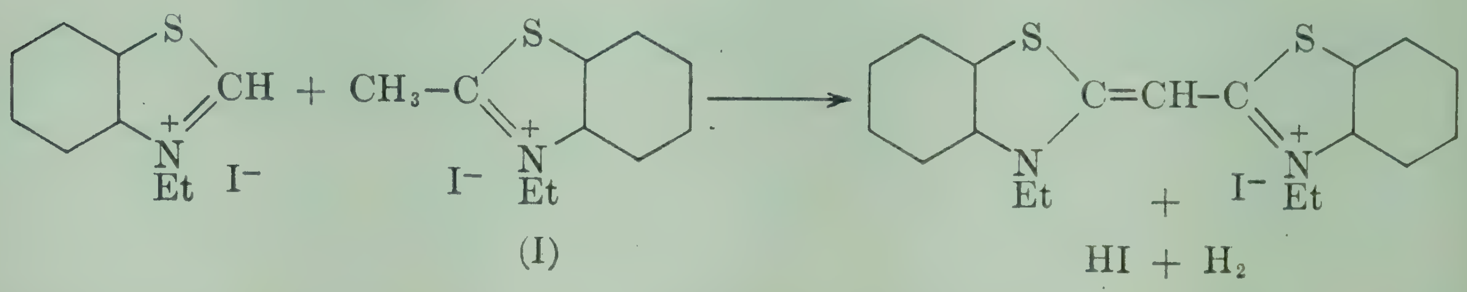


(X)

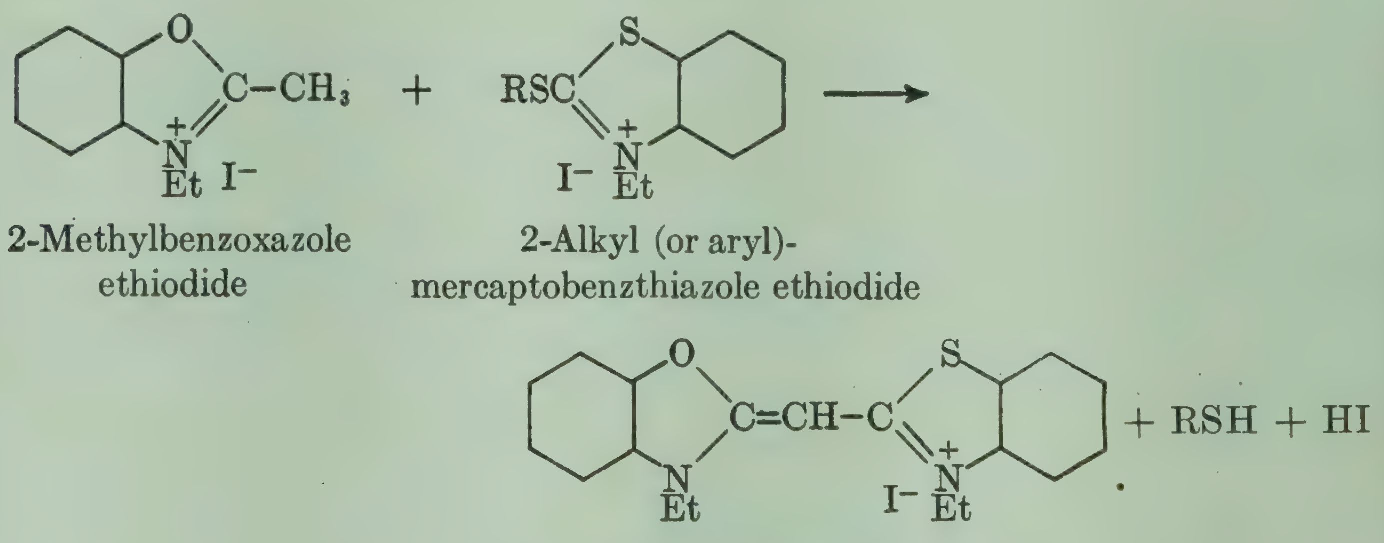
and the number of methine groups are all indicated. Thus the dye (X) is named 3,3′-diethyloxathiadicarbocyanine iodide in the first system, and [3-ethylbenzoxazole-(2)]-[3-ethylbenzothiazole-(2)] pentamethinecyanine iodide in the Beilstein system.

Benzothiazole Derivatives

Among the heterocyclic nuclei other than quinoline, the most widely studied is benzothiazole and general methods of preparation, additional to those described for quinoline derivatives, are therefore discussed in this section. The yellow 3,3′-diethylthiacyanine iodide together with the crimson thiacarbocyanine was isolated by Mills from the products of the action of pyridine on a mixture of benzothiazole ethiodide and 2-methylbenzothiazole ethiodide (I); and the constitution was proved by synthesis from *o*-aminothiophenol and diethyl malonate.[31] A greatly improved method was discovered by Kendall, in which 2-alkylmercaptobenzothiazoles are used as intermediates and alkyl *p*-toluenesulfonates as quaternary salt-forming agents; Hamer has shown that the same alkyl group must be present in the alkylthiol group and in the salt-forming agent since a rearrangement can occur; this reaction, which is of wide utility for the synthesis of both symmetrical and unsymmetrical benzothiazole derivatives, is illustrated for an oxathiacyanine.[32, 33] By condensing a 2-alkylmercaptobenzothiazole alkiodide with 2- or 4-methylquinoline a base is obtained; some of these bases, as well as their quaternary salts, have sensitizing properties.[32, 33a]



(I)



2-Methylbenzoxazole ethiodide

2-Alkyl (or aryl)-mercaptobenzthiazole ethiodide

3,3′-Diethyloxathiacyanine iodide

Thiacarbocyanines constitute a series of useful sensitizers. By heating a 2-methylbenzothiazole alkyl halide with ethyl orthoformate in

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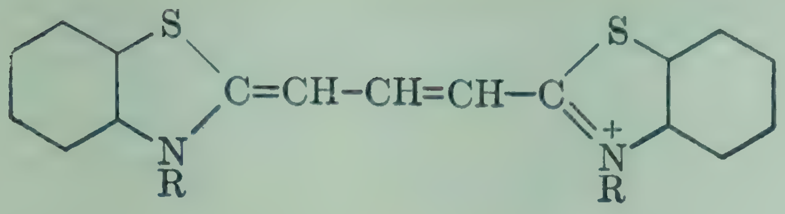
[31] *JCS* **121,** 455 (1922). See also Hofmann, *Ber.* **20,** 2251 (1887).

[32] Kendall, BP 424,559; 425,609; 438,420; 456,362; 477,983; Kendall and Suggate, *JCS* 1503 (**1949**); Hamer, *JCS* 799 (**1940**); see also IG, BP 423,792; Kendall, BP 431,141.

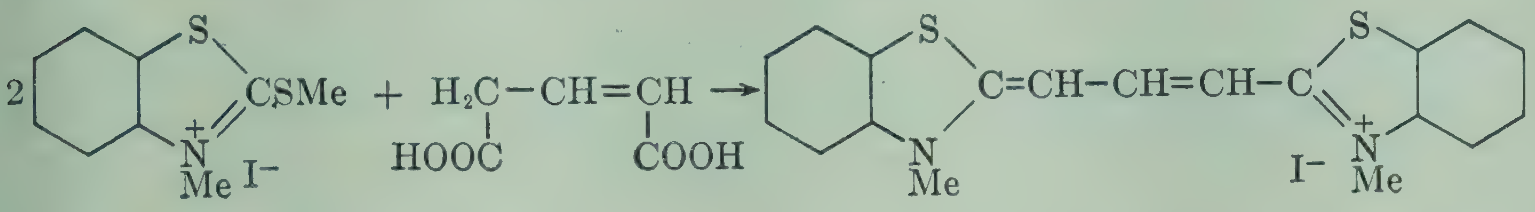
[33] Brooker and Keyes, USP 2,117,936; Brooker, USP 2,202,827; 2,231,657.

[33a] See also Brooker, Sprague, and Eastman Kodak, USP 2,345,094; 2,393,743.

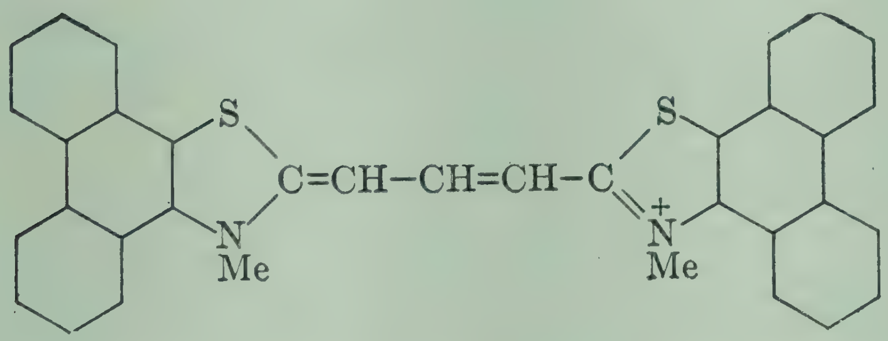


Thiacarbocyanine

pyridine, crimson thiacarbocyanines are obtained. These are powerful green sensitizers. Another route[34] to thiacarbocyanines is the condensation of a mercaptobenzothiazole with glutaconic acid or crotonic anhydride. A cyanine derived from phenanthrathiazole is (II), used by Agfa in the top coat of a roll film.[35]

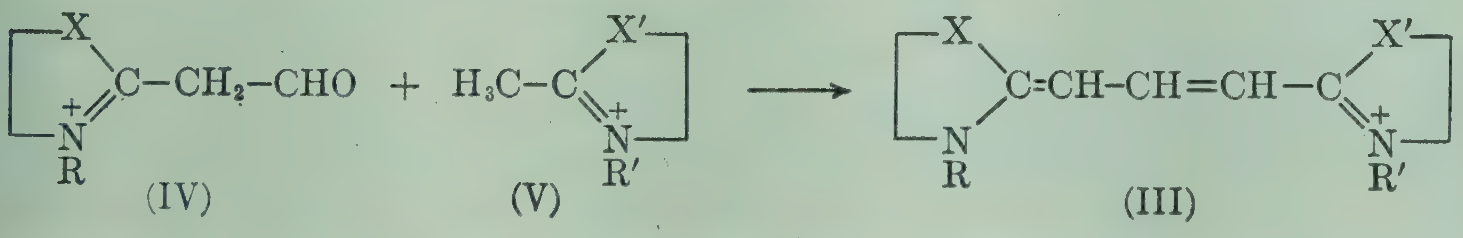


3,3′-Dimethylthiacarbocyanine iodide



(II)

Unsymmetrical carbocyanines (III) are of great technical importance and methods for their synthesis have been extensively investigated. The requirement for producing an unsymmetrical carbocyanine of authentic structure is to effect the synthesis in two stages; the ω-aldehyde (IV) (or a derivative or equivalent) is first prepared and subsequently condensed with (V) in acetic anhydride or pyridine solution. The aldehyde group in (IV) can be introduced by treatment of the appropriate heterocyclic compound having a reactive 2-methyl or methylene group with formylating agents such as *N*-methylformanilide in presence of phosphorus oxychloride or phosgene.[36] Knott has shown that alkyl



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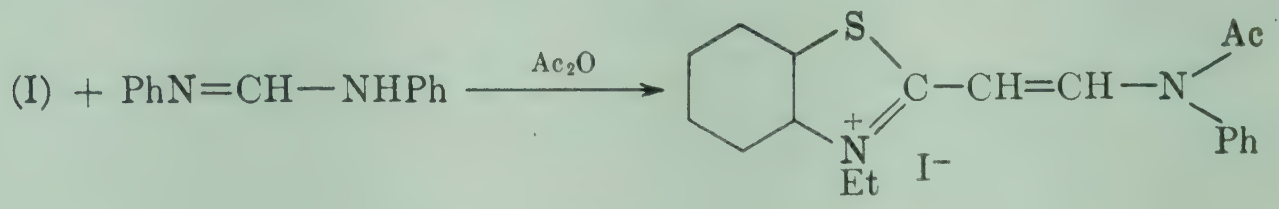
[34] Kendall, BP 431,186.

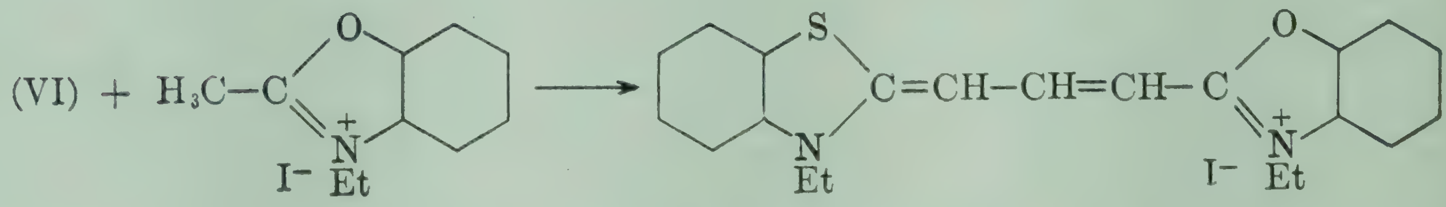
[35] *FIAT* **354-360**; a dye of this type with Et instead of Me was described by Keyes and Brooker, *JACS* **59,** 74 (1937).

[36] IG, BP 438,278; 506,797; see also Ciba, BP 334,706; Eastman Kodak, BP 466,245; Knott and Eastman Kodak, BP 577,548–9; Knott, *JCS* 120 (**1946**); *ibid.* 687 (**1945**); USP 2,487,882.

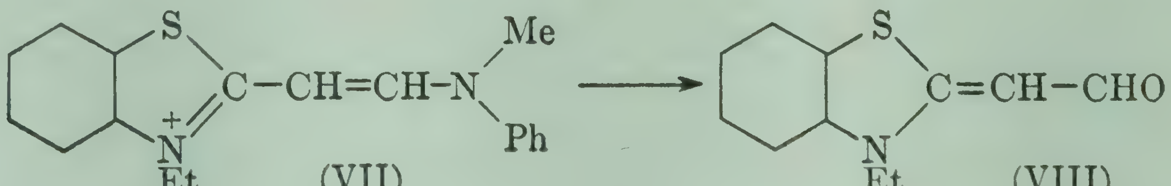
isoformanilide (alkoxymethyleneaniline; PhN=CHOR) gives a good yield of the anil of (IV) in the form of the β-anilinovinyl compound $(-CH_2CH{=}NPh \rightleftarrows -CH{=}CH{-}NHPh)$.[36] The condensation of (IV) with (V) can be facilitated by converting (IV) into derivatives such as the semicarbazones[37] or the thioaldehydes.[38] Thioaldehyde and thioketonic derivatives of the usual 2-methyl intermediates for cyanine dyes can be prepared by treating the appropriate aldehyde or ketone with phosphorus pentasulfide in pyridine.[39] A valuable general method for the synthesis of unsymmetrical carbocyanines involves the use of diphenylformamidine.[40] Acetic anhydride plays an important part in



(VI)

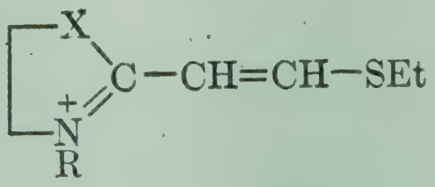


the synthesis, since the *N*-acetyl derivative (VI) of the intermediate product gives a much higher yield than the unacetylated compound.[41] Using an *N*-alkyl diphenylformamidine in this reaction, the intermediate compound (e.g. VII) can be hydrolyzed by aqueous caustic soda to the



(VII) (VIII)

ω-aldehyde (VIII).[42] Another useful general reaction is to condense the quaternary alkyl *p*-toluenesulfonates of heterocyclic bases containing reactive methyl or methylene groups with esters of trithioorthoformic acid in acetic anhydride solution. The intermediate 2-β-ethylthiovinyl



(IX)

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[37] IG, BP 486,780; 510,242.

[38] Kumetat and Riester, USP 2,349,179; 2,354,524.

[39] Brooker, Keyes, and Eastman Kodak, BP 566,010; Smet and Mees, USP 2,356,509.

[40] Piggott, Rodd and ICI, USP 2,071,898–9; BP 344,409; 353,863; 354,898. See also Knott, BP 609,814.

[41] Ogata, *Proc. Imp. Acad. Tokyo* **13**, 325 (1937).

[42] IG, BP 486,780.

compound (IX) is then condensed with the usual type of 2-methyl compound (e.g. I) to obtain the desired carbocyanine.[43]

The diphenylformamidine method for the synthesis of an unsymmetrical carbocyanine, in which one component is a benzothiazole and the other is a quinoline, is illustrated by Ma 2116 (IG) (Chart 1); this dye has its sensitizing maximum at 7050A.[44] The condensation of *N*-ethyl-2,5,6-trimethylbenzothiazole ethosulfate with diphenylformamidine is effected by heating the two in acetic acid-anhydride solution on the waterbath for 30 minutes. Dilution with ethyl acetate gives (X), from which the base (XI) is liberated by heating with aqueous caustic soda.

Brooker has described a series of *N*,*N*-diaryl-cyanine and -thiacarbocyanine dyes. 3-Phenyl-2-methylbenzothiazolium iodide, intermediate for this type of thiacarbocyanines, is prepared by oxidizing *N*,*N*-diphenylthioacetamide with iodine.[45] Kiprianov and Ushenko describe a simplified procedure for the preparation of *N*-phenylbenzothiazoles; a benzene solution of 2-mercaptodiphenylamine is treated with an acyl chloride, when the corresponding 2-alkyl-3-phenylbenzothiazolium chloride separates immediately, and this is readily converted into the iodide. Cyanine dyes have been prepared from the 2-methyl derivative, and the *N*-phenyl group has a strong bathochromic effect.[45]

Symmetrical and unsymmetrical carbocyanines with an alkyl or other substituent in the methine chain have been prepared by several methods and some are useful sensitizers. Brooker and White have shown that a thiacarbocyanine with a methyl attached to the middle methine group can be obtained in 56% yield by heating (I) with pyridine and triethylamine, the central =CMe— group being provided by the breakdown of the thiazole ring in (I).[46] A further method for the synthesis of symmetrical carbocyanines with an alkyl attached to the middle methine group is to replace ethyl orthoformate by the orthoacetate and similar esters for the condensation of compounds of the type of (I), although the reaction does not proceed with all such quaternary salts.[47] For the preparation of unsymmetrical carbocyanines such as (XIV), (I) s treated with acetyl chloride in pyridine, and the product (XII) is condensed with a quaternary salt such as (XIII) in acetic anhydride to

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[3] Kendall and Majer, *JCS* 687 (**1948**); USP 2,438,705. For other methods of preparing cyanine dyes see BP 629,106; 629,122; 639,758; 640,127.

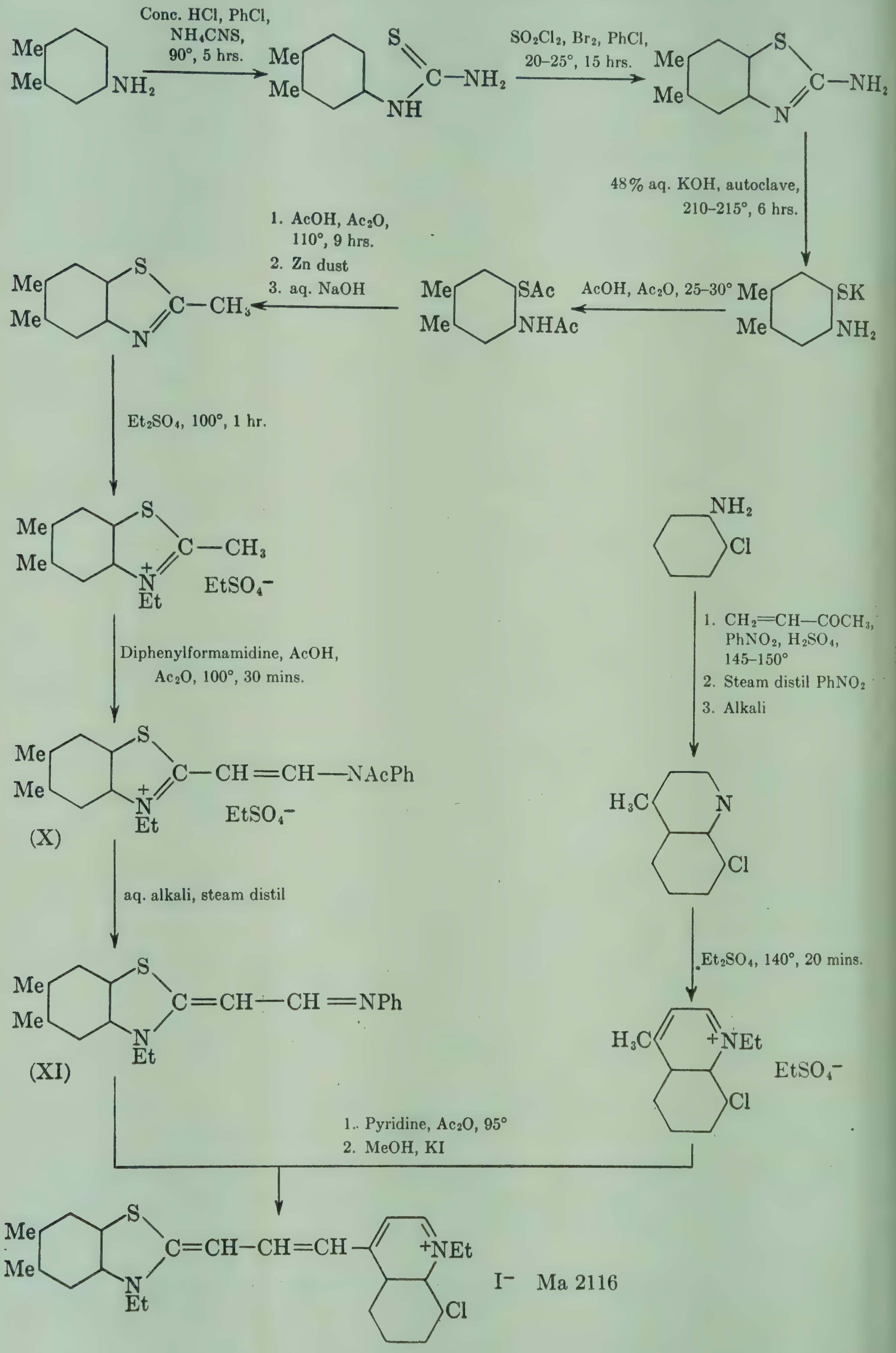
[4] *FIAT* **943.**

[5] Brooker, Williams and Eastman Kodak, BP 551,330–1; 551,824; 552,309; BP 618,073; USP 2,317,357; Kiprianov and Ushenko, *J. Gen. Chem. U.S.S.R.* **17,** 2201 (1947).

[6] *JACS* **57,** 547 (1935).

[7] Hamer, *JCS* 3160 (**1928**); Brooker and White, *JACS* **57,** 2480 (1935).

CHART 1
Preparation of Ma 2116


Conc. HCl, PhCl, NH_4CNS, 90°, 5 hrs.
SO_2Cl_2, Br_2, PhCl, 20–25°, 15 hrs.
48% aq. KOH, autoclave, 210–215°, 6 hrs.
AcOH, Ac_2O, 25–30°
1. AcOH, Ac_2O, 110°, 9 hrs.
2. Zn dust
3. aq. NaOH
Et_2SO_4, 100°, 1 hr.
Diphenylformamidine, AcOH, Ac_2O, 100°, 30 mins.
(X)
aq. alkali, steam distil
(XI)
1. $CH_2{=}CH{-}COCH_3$, $PhNO_2$, H_2SO_4, 145–150°
2. Steam distil $PhNO_2$
3. Alkali
Et_2SO_4, 140°, 20 mins.
1. Pyridine, Ac_2O, 95°
2. MeOH, KI
I^- Ma 2116

form the cyanine dye (XIV).[48] The ketone (XII) can be converted into the corresponding thioketone and then condensed with (XIII). Another method of linking up two components such as (I) and (XIII) to form (XIV) is to use ethylisothioacetanilide (EtS—CMe=NPh).[49] Rr 1650 (IG), which has its sensitizing maximum at 5550–5600A, is an oxathiacarbocyanine with a branch methyl group, prepared by the use of ethyl isothioacetanilide (Chart 2).[44] A thiacarbocyanine with a branch

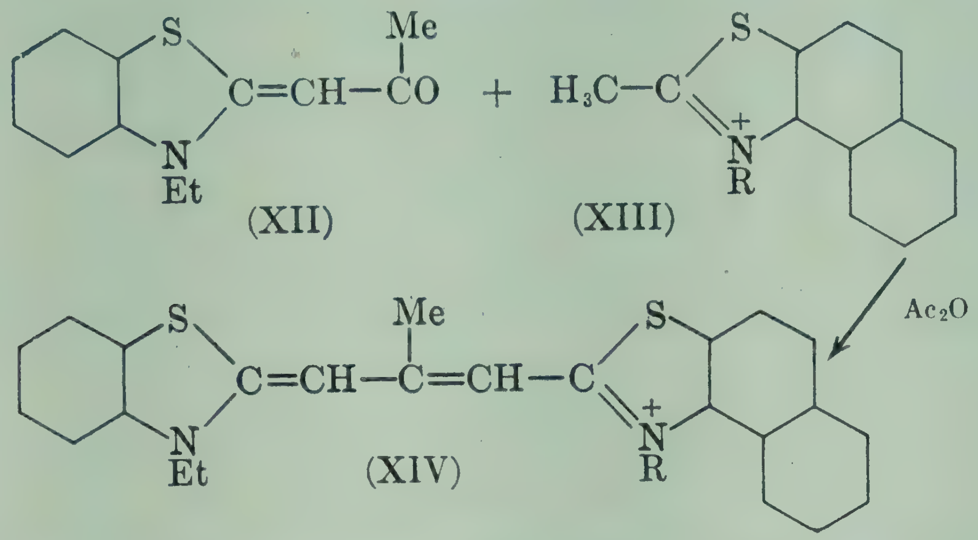
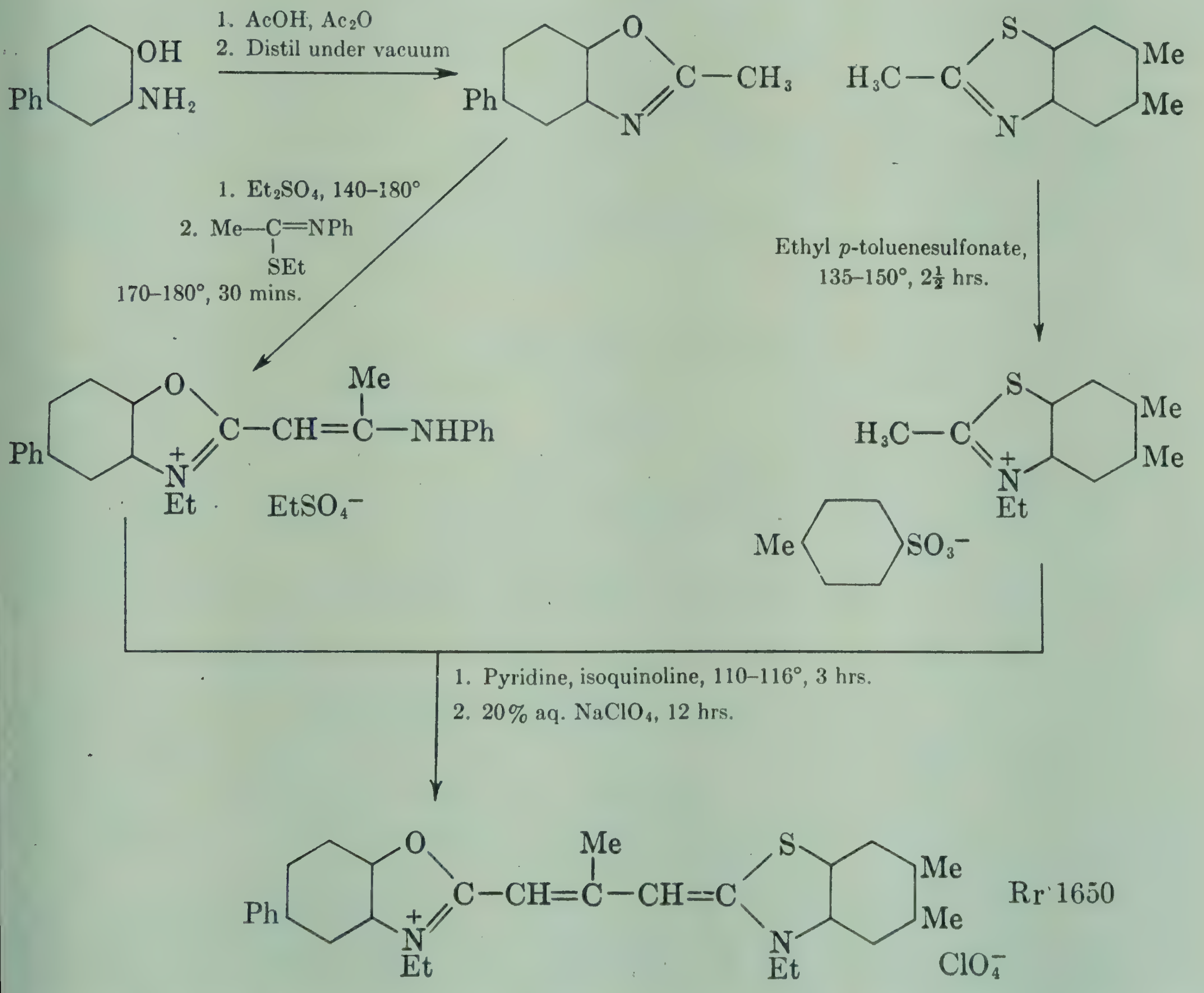

(XII) (XIII) (XIV)

CHART 2

PREPARATION OF RR 1650


1. AcOH, Ac₂O
2. Distil under vacuum
1. Et₂SO₄, 140–180°
2. Me—C=NPh, SEt
170–180°, 30 mins.
Ethyl p-toluenesulfonate, 135–150°, 2½ hrs.
1. Pyridine, isoquinoline, 110–116°, 3 hrs.
2. 20% aq. NaClO₄, 12 hrs.
Rr 1650

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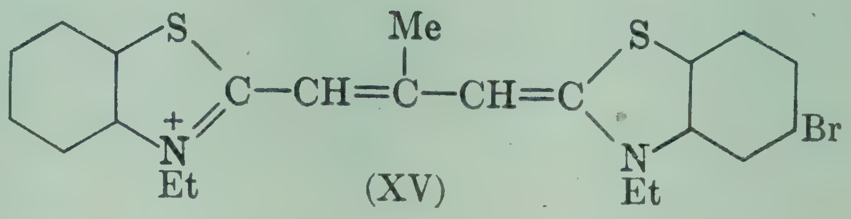
[8] Brooker, White, and Eastman Kodak, 2,112,139–40; 2,369,646–7; 2,441,529; BP 466,246; 466,269.

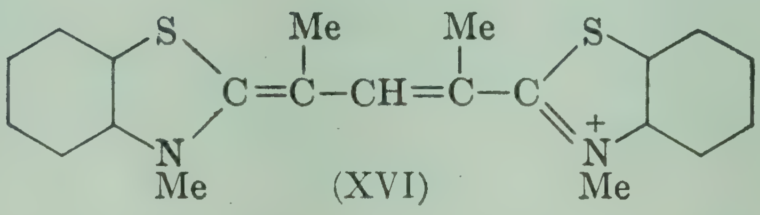
[9] IG, BP 412,309; Koslowsky, USP 2,107,379.

methyl in the carbon chain, used by Agfa in the undercoat of a roll film, is (XV).[35]


(XV)

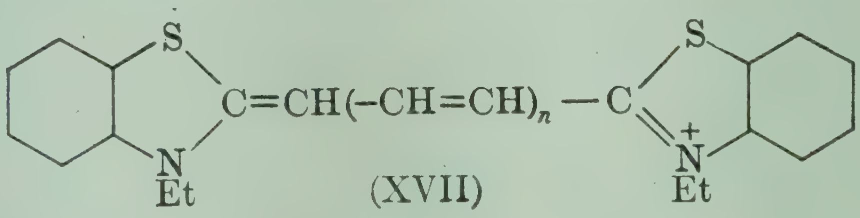
Symmetrical carbocyanines with an *o*-carboxyphenyl or β-carboxyethyl substituent on the *meso*-carbon atom have been prepared by condensing (I) and its analogs with phthalic or succinic anhydride.[49a] Substitution of an alkylmercapto group at the central C atom of an unsymmetrical carbocyanine yields a dye with very high sensitizing action.[49b]

By condensing 2-ethylbenzothiazole methiodide with ethyl orthoformate, an 8,10-dimethylthiacarbocyanine (XVI) can be prepared; and

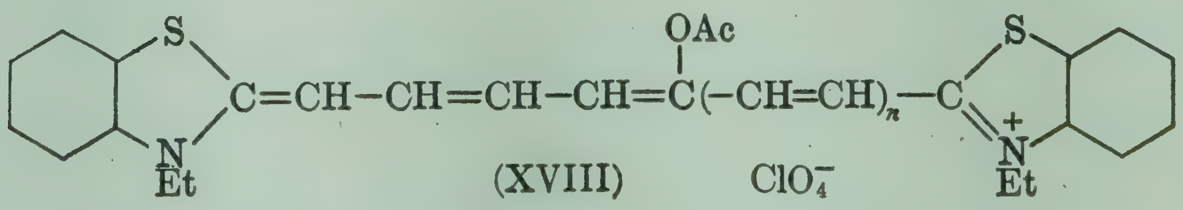

(XVI)

analogous dyes containing other substituents in the end methine groups can be prepared by using suitable intermediates for the ethyl orthoformate condensation.[50] Carbocyanines in which one or both the α-carbon atoms carry an alkoxy or aryloxy group absorb more in the red.[50]

Thiapolycarbocyanines (XVII) in which n varies from 2 to 5 have been prepared, the color deepening in the expected manner[2] as the length


(XVII)

of the carbon chain increases. The absorption and sensitizing spectra of a series of dyes of the formulas (XVII) and (XVIII)[29] are shown in Fig. 2. The shifts in wave length between successive maxima are about


(XVIII)

[49a] Brooker, Sprague, and Eastman Kodak, USP 2,226,156.

[49b] Gevaert Photo-Producten, BP 623,990.

[50] König, Kleist and Götze, *Ber.* **64,** 1664 (1931); Zeh and Schneider, USP 2,065,411; Brooker, USP 2,060,023; Brooker, White and Eastman Kodak, BP 592,267; USP 2,478,366.

1000A.[1] Soloviev has found that the adsorption of a vinylene series of thiacyanines by silver bromide increases regularly with increasing chain length. The maximum of sensitizing is displaced towards the long wave length and the concentration of dye corresponding to optimum sensitizing decreases (together with an increase in fog), as the chain length increases.[51] The thiatetracarbocyanine (XVII; $n = 4$) has its sensitizing maximum at about 9400A, and the thiapentacarbocyanine (XVII; $n = 5$) at about 10500A. The thiapentacarbocyanines from the naphthothiazoles sensitize with maxima at about 10900A, but lines have been photographed beyond 13000A with their aid.[25, 29] Photographic plates sensitive to the infrared to 13000A have been produced commercially, and the spectrum of the sun has been mapped to about 13600A (Babcock; Herzberg).[26]

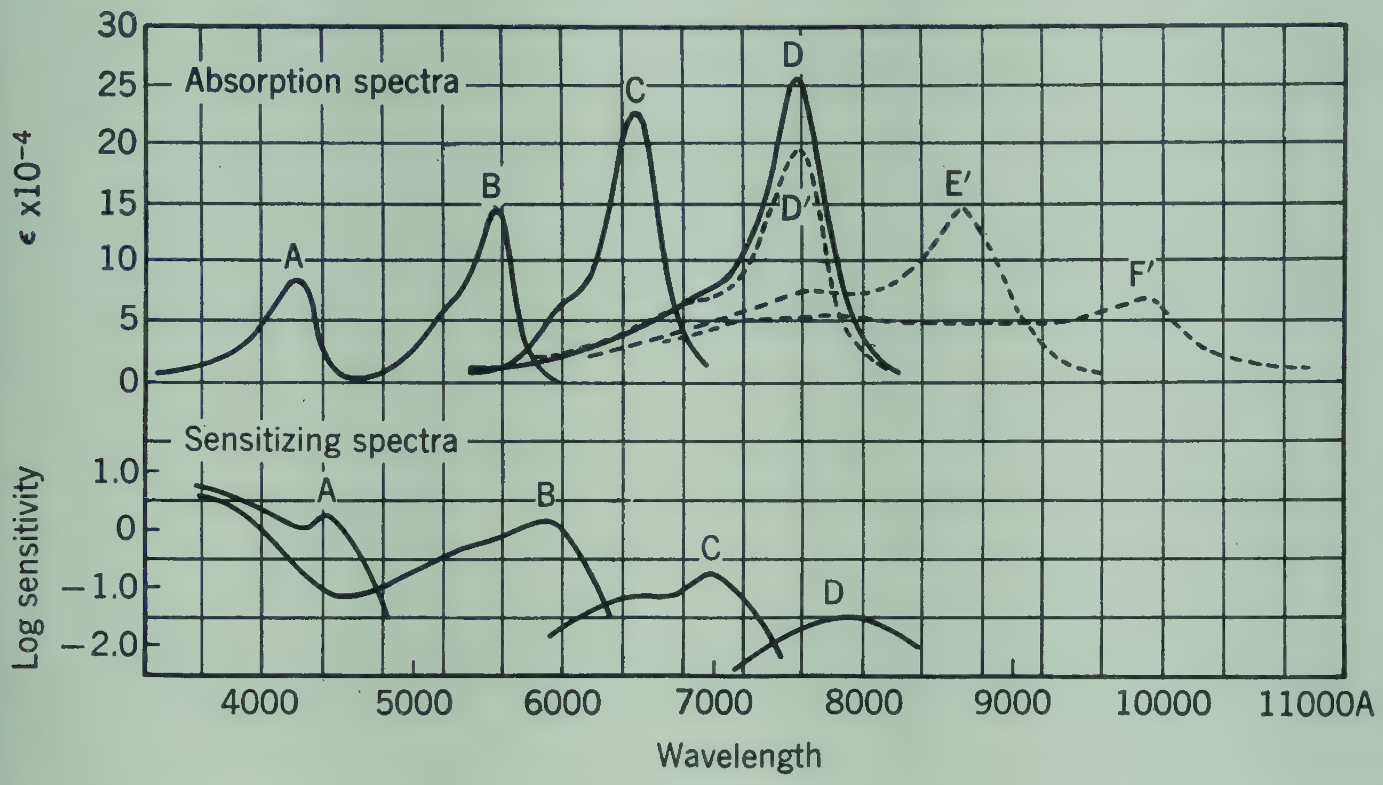


Fig. 2. Absorption spectra of dyes dissolved in methanol; A, B, C, D, dyes of the structure (XVII) when $n = 0, 1, 2, 3$, respectively; D′, E′, F′, dyes of formula (XVIII) when $n = 1, 2, 3$, respectively. Sensitization curves for dyed silver chloride emulsion: A, B, C, D correspond to the sensitivities conferred by dyes of formula (XVII) when $n = 0, 1, 2, 3$, respectively (Brooker).

The replacement of ethyl orthoformate in the carbocyanine synthesis by β-ethoxyacrolein acetal leads to a dicarbocyanine.[52] A β-alkylmercaptoacrolein dialkyl mercaptal of the general formula $RSCH{=}CHCH(SR)_2$ may be used in place of β-ethoxyacrolein acetal; the reactants are refluxed in pyridine solution for 15 minutes.[53] Another route to symmetrical dicarbocyanines is exemplified by the preparation of thiadicarbocyanine from 2-alkylmercaptobenzothiazole alkiodide and sorbic anhydride.[34] The condensation of (IX) with cyanoacetic acid gives a

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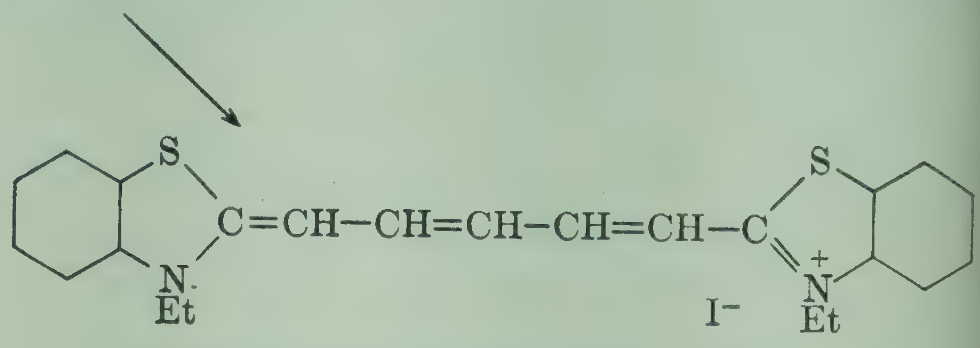
[51] *J. Phys. Chem. U.S.S.R.* **19,** 451 (1945).

[52] König, USP 1,524,791.

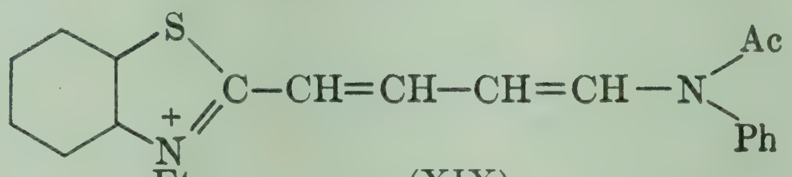
[53] Kendall *et al.*, USP 2,412,814–6; BP 553,143–4; see also Eastman Kodak, BP 555,266.

$2\ (I) + EtO{-}CH{=}CH{-}CH{=}(OEt)_2$



3,3′-Diethylthiadicarbocyanine iodide

dicarbocyanine with a *meso* cyanomethine group.[53a] Unsymmetrical dicarbocyanines can be prepared by condensing (I) with β-anilinoacrolein



(XIX)

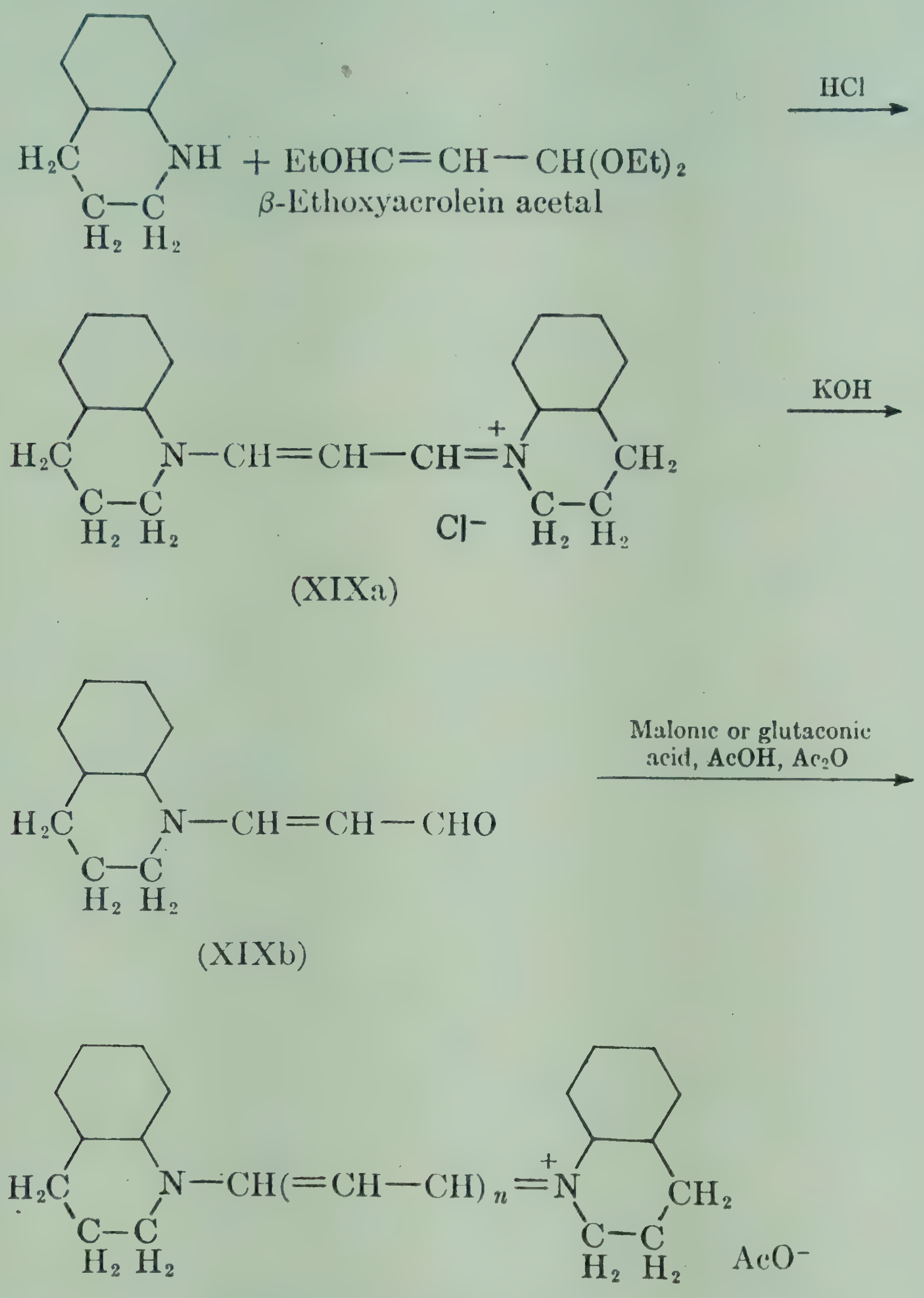
anil (PhNHCH=CH—CH=NPh) in acetic anhydride to form (XIX), which is then condensed with a quaternary salt having a reactive 2-methyl or methylene group.[54] Symmetrical and unsymmetrical tricarbocyanines can be prepared by using glutaconaldehyde dianil hydrochloride.[27]

The compounds with 9- and 11-carbon chains are difficult to synthesize and are unstable;[29, 30] but the stability is improved when they are converted into the perchlorates. Tetra- and pentacarbocyanines (XVII) without the acetoxy substituent have been stated to be more stable than (XVIII) and to have superior sensitizing properties, and a method for their preparation has been outlined by Dieterle and Riester.[30] The method consists in the condensation of tetrahydroquinoline with β-ethoxyacrolein acetal, hydrolysis of the product (XIXa) with alkali to tetrahydroquinolylacrolein (XIXb), condensation of (XIXb) with malonic or glutaconic acid, and final condensation of the bis-tetrahydroquinolide (XIXc) with quinaldine alkiodide. The dyes (XVIII) are prepared by König's extension of the glutaconaldehyde method for the preparation of tricarbocyanines; the dianil hydrobromide obtained by the action of aniline and hydrobromic acid on furfural or the appropriate vinylene homolog is condensed with 2-methylbenzothiazole ethiodide.[29]

[53a] Doyle, Kendall, and Ilford Ltd. BP 620,801–2; USP 2,471,488.

[54] Piggott, Rodd, and ICI, BP 355,693; IG, BP 434,234–5; Zeh, USP 2,131,865. For other modifications of the general reactions for the preparation of unsymmetrical pentamethinecyanines, see Sprague, and Eastman Kodak, USP 2,269,234; Kendall and Edwards, BP 562,565–8; Hamer, *JCS* 32 (**1949**).

The *O*-acetyl group in (XVIII) makes the dyes more stable than the hydroxy compounds.



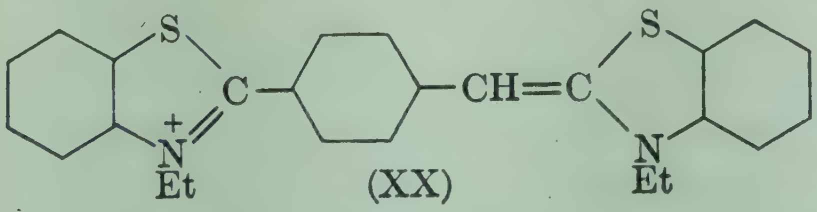
HCl
β-Ethoxyacrolein acetal
KOH
Malonic or glutaconic acid, AcOH, Ac₂O

(XIXa)

(XIXb)

(XIXc; *n* = 3 or 4)

The numerous variations that are possible in the structure of cyanine dyes may be illustrated by a few further examples of thiazole derivatives. The dye (XX) represents a type in which four of the carbon atoms of a

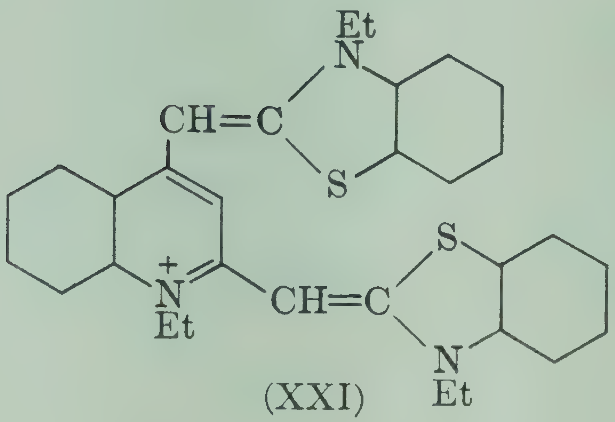


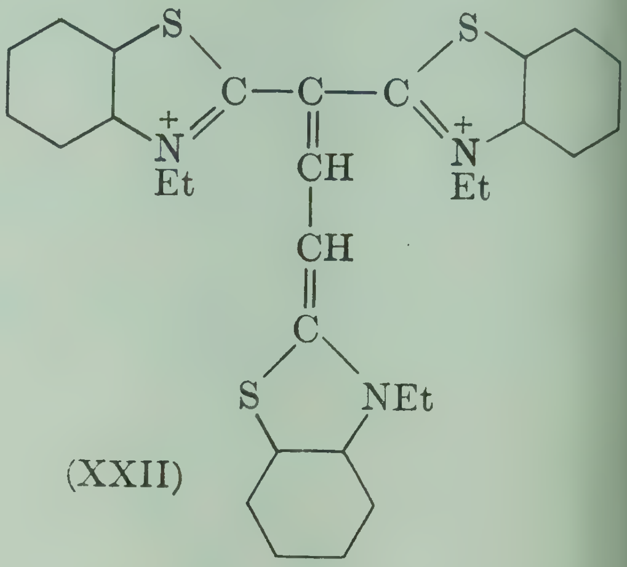
(XX)

enzene ring form part of the methine chain joining the nitrogen atoms a thiadicarbocyanine. It is obtained by the action of ammonia on -(*p*-2′-benzothiazolylbenzyl)benzothiazole diethiodide.[55]

Brooker, Sprague, and Eastman Kodak, USP 2,356,445; Kiprianov *et al.*, *J. Gen. Chem. U.S.S.R.* **14,** 865 (1944).

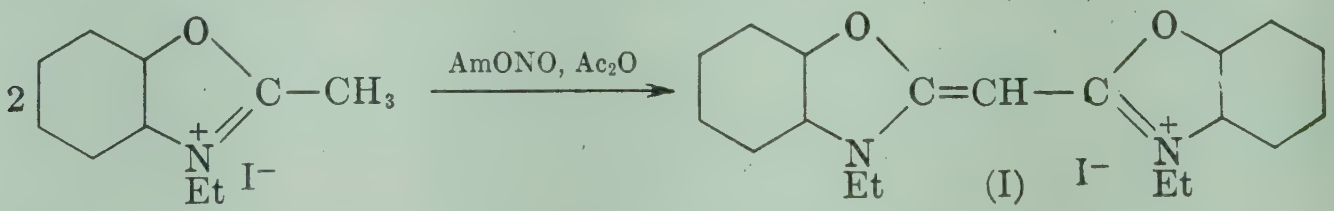
Neocyanine is one example of a trinuclear cyanine dye; and another type of trinuclear cyanine is represented by (XXI) prepared by the condensation of 2-methylbenzothiazole etho-*p*-toluenesulfonate (2 mols) with 2,4-diiodoquinoline ethiodide.[56] It is a good sensitizer and if a silver chloride emulsion is sensitized with the dye, the sensitivity curve shows two distinct peaks at about 4500A and 5500A, which are closely related to the absorption maxima.[1] The dye (XXII) is an example of a new class of trinuclear cyanine, in which two nitrogen atoms are quaternized; (XXII) is prepared by heating 2,2′-dibenzothiazolylmethane with 2-(β-methylmercapto)vinylbenzothiazole ethioide in pyridine containing a little triethylamine.[56a] The *C*-methyl group in (XV) can condense with aldehydes or with quaternary ammonium salts of heterocyclic compounds containing an alkylthiol group in a reactive position (e.g., ω-methylmercaptoquinaldine ethiodide) to form trinuclear cyanine dyes.[57]


(XXI)


(XXII)

Benzoxazole Derivatives

The oxacyanine (I) is of interest, since it was the first colorless cyanine to be synthesized. The synthetic method[58] had already proved useful in the thiacyanine and indocyanine series;[59] it consists in treating a quaternary salt containing a reactive methyl group (e.g., 2-methyl-



(I)

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[56] Brooker and Smith, *JACS* **59,** 67 (1937).

[56a] Anish and General Aniline and Film, USP 2,427,177; 2,432,060.

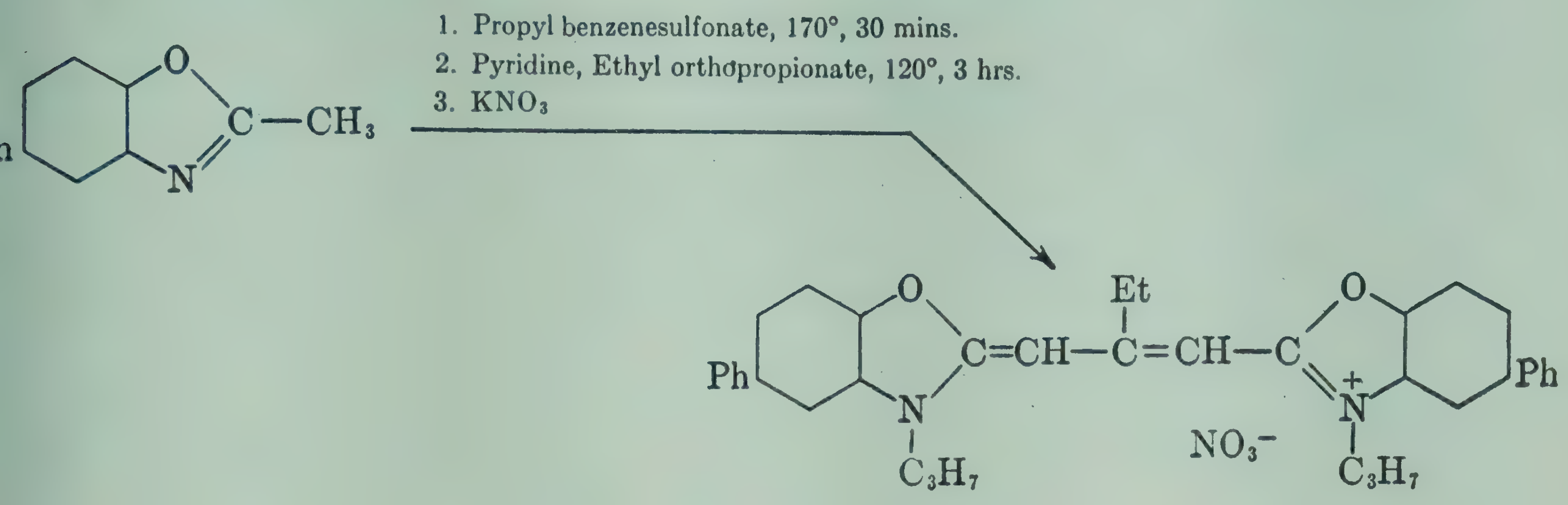
[57] Ogata, *Bull. Chem Soc. Japan* **11,** 262 (1936); Brooker, White and Eastman Kodak, USP 2,282,115.

[58] Fisher and Hamer, *JCS* 962 (**1934**).

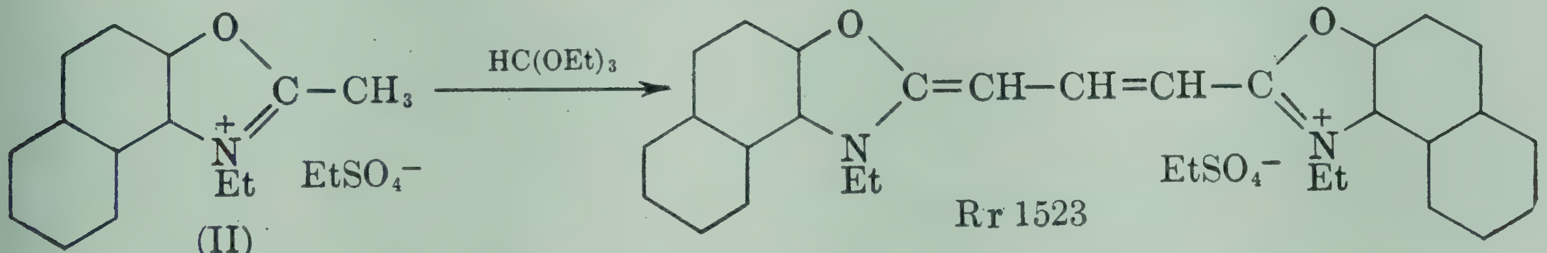
[59] Kuhn, Winterstein, and Balser, *Ber.* **63,** 3176 (1930); Fisher and Hamer, *JCS* 2502 (**1930**); IG, BP 380,702.

benzoxazole ethiodide) in boiling acetic anhydride with amyl nitrite, and cooling.

Bau 2000 (IG) is made by the indicated reaction and its sensitizing maximum is at 5450–5500A.[44] Rr 340 (IG), an analog of Bau 2000 in which the *N*-alkyl groups are Et instead of Pr, has its sensitizing maximum in the same range.[44] A third example of an oxacarbocyanine is Rr 1523 (IG), prepared by treating 2-methylnaphthoxazole ethosulfate (II) with ethyl orthoformate in boiling pyridine for 8 hours.[44] The dye has its sensitizing maximum at 5250A.


1. Propyl benzenesulfonate, 170°, 30 mins.
2. Pyridine, Ethyl orthopropionate, 120°, 3 hrs.
3. KNO₃

Bau 2000



(II)

Rr 1523

BENZOSELENAZOLE DERIVATIVES

Kt 945 (IG), which has its sensitizing maximum at 5550–5600A, is a good example of the method of synthesis of a mixed carbocyanine in which one component is a benzoselenazole and the other is a benzimidazole (Chart 3).[44, 59a] The imidazole (I) is prepared by acetylating the *o*-phenylenediamine derivative (II) with acetic anhydride, distilling off excess acetic anhydride and distilling the residual acetyl derivative (III) at 254°/4–5 mm. The distillate solidifies on cooling. The selenazole (IV) is prepared from diazotized *o*-nitraniline, which is neutralized with sodium acetate and treated with potassium selenocyanate solution at 0°. Reduction of *o*-nitrophenylselenocyanate with alcoholic caustic soda and hydrosulfite gives 2,2′-diaminodiphenyldiselenide, which is heated with zinc dust and acetic anhydride at 100° for 20 hours to give 2-methyl-

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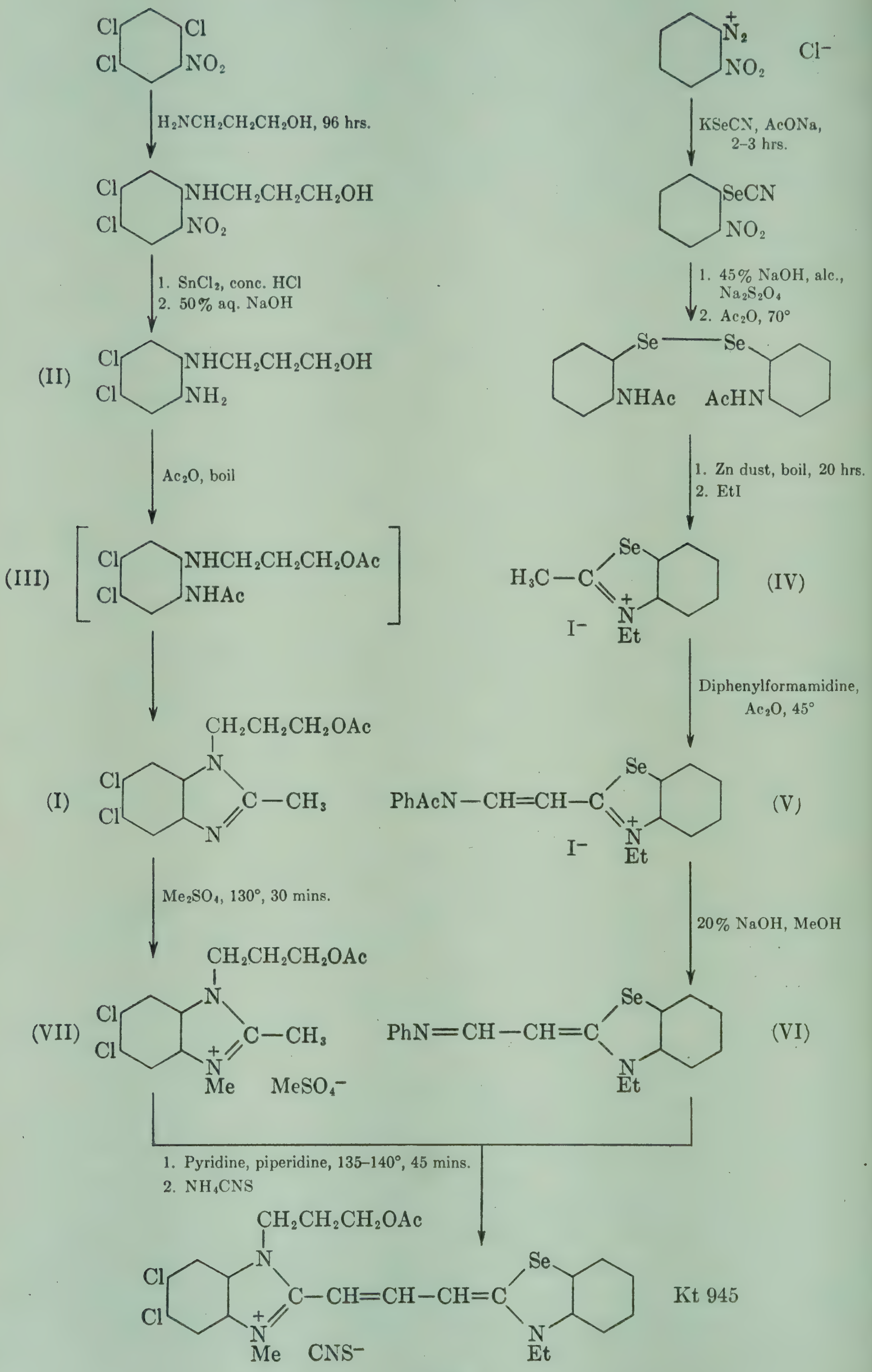
[59a] For the preparation of cyanine dyes containing the naphtho[1,2]selenazole nucleus, see Cressman and Eastman Kodak, BP 610,566.

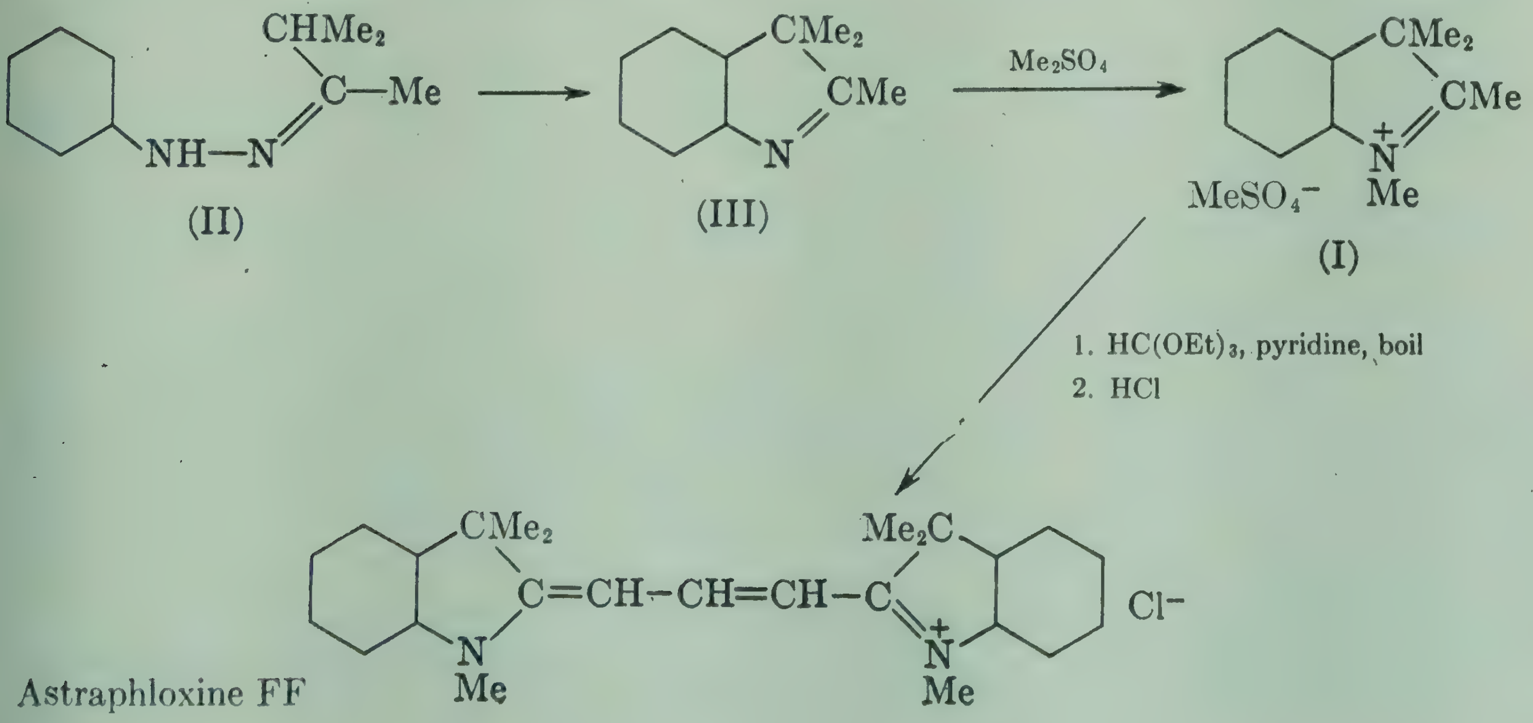
CHART 3
Preparation of Kt 945


H₂NCH₂CH₂CH₂OH, 96 hrs.
1. SnCl₂, conc. HCl
2. 50% aq. NaOH
(II)
Ac₂O, boil
(III)
(I)
Me₂SO₄, 130°, 30 mins.
(VII)
MeSO₄⁻
KSeCN, AcONa, 2–3 hrs.
1. 45% NaOH, alc., Na₂S₂O₄
2. Ac₂O, 70°
1. Zn dust, boil, 20 hrs.
2. EtI
(IV)
Diphenylformamidine, Ac₂O, 45°
(V)
20% NaOH, MeOH
(VI)
1. Pyridine, piperidine, 135–140°, 45 mins.
2. NH₄CNS
CNS⁻
Kt 945

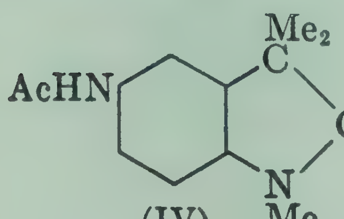
benzoselenazole. The ethiodide (IV) is then condensed with diphenylformamidine in acetic anhydride at 45–95° during 10 minutes, and the product (V) precipitated by alcohol-ether. The base (VI) is liberated by boiling methanolic caustic soda and steam-distilled; the oily distillate is taken up in benzene, clarified with charcoal and the solution concentrated, when yellow crystals separate on cooling. This material is further purified by dissolving in chloroform (charcoal), adding toluene, cooling, and shaking with water, when yellow crystals are obtained. For the condensation of (I) and (VI) to form the cyanine dye, (I) is first converted into the imidazole methosulfate (VII) by heating with dimethyl sulfate at 130°. The reaction product is then heated with pyridine, piperidine and (VI) at 135–140° for 45 minutes. On cooling and adding 20% aqueous ammonium thiocyanate solution, the dye slowly crystallizes out, and is recrystallized from methanol-ether.

INDOCARBOCYANINES

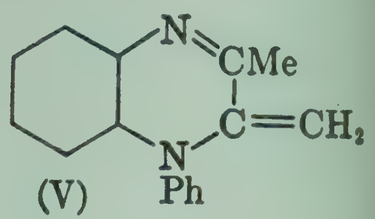
By using indolenine derivatives, cyanine dyes are obtained, which have a limited use, not as photographic sensitizers, but as coloring matters for textiles. Astraphloxine FF (IG) (König, 1922), prepared from 2,3,3-trimethylindolenine methosulfate (I) by the general ethyl orthoformate method for carbocyanines, is a beautiful bright red basic dye, which is valued in calico printing. The indolenine intermediates can be prepared by applications of the Fischer indole synthesis. The action of condensing agents (zinc chloride, hydrochloric acid or sulfuric acid) on the phenylhydrazone (II) of methyl isopropyl ketone leads to the indolenine (III), from which (I) is obtained by treatment with dimethyl sulfate. A second route is to carry out the Fischer synthesis on the phenylhydrazone of methyl ethyl ketone, and methylate the resultant 2,3-dimethylindole by means of methyl bromide in methanol. Like



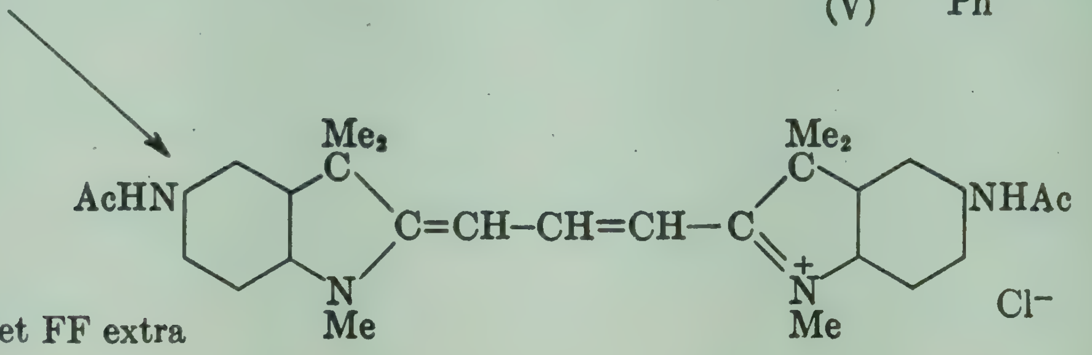
other basic colors, Astraphloxine FF is not fast to light, but because of the clarity of the shade and the good fastness to washing and alkali, the range has been extended. An example is Astra Violet FF extra (IG) which is made by treating the 5-acetamido derivative of (I) or the corresponding base (IV) with sodium formate and acetic anhydride at 30° for several hours, pouring into dilute hydrochloric acid and salting out.[60, 61] The symmetrical trimethine dye from the quinoxaline derivative (V) has been stated to dye tannin-mordanted cotton in green shades fast to acid and alkali.[62]



(IV)



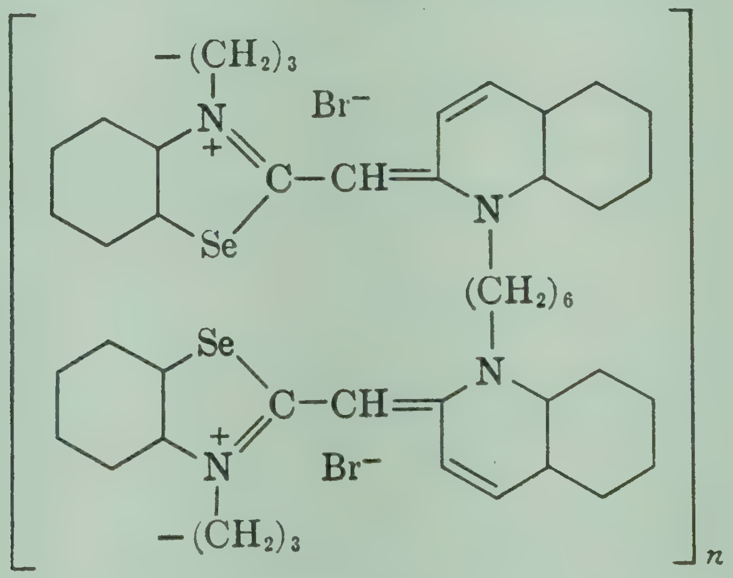
(V)



Astra Violet FF extra

Miscellaneous Cyanine Types

Methylenedioxy groups in the thiazole or selenazole nuclei of cyanines are claimed to give much stronger absorption by the silver halide grains and to prevent the wandering of the dyes to adjacent layers.[63] A recent innovation is the production of polymeric cyanine dyes such as



(I)

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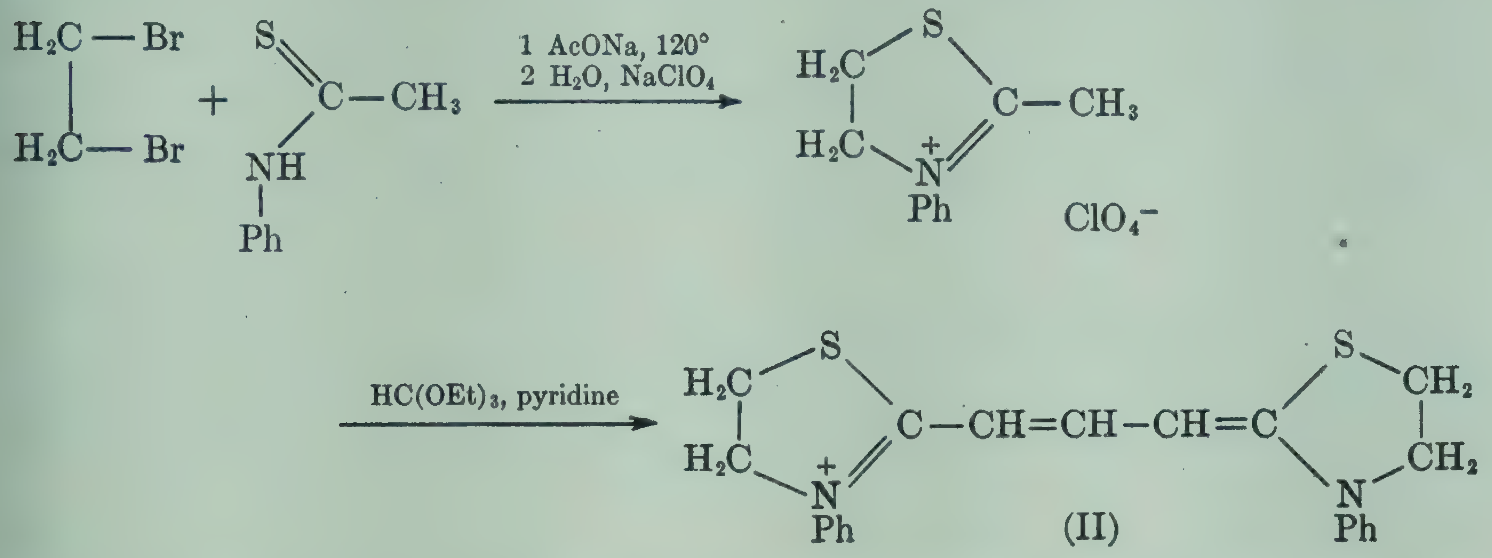
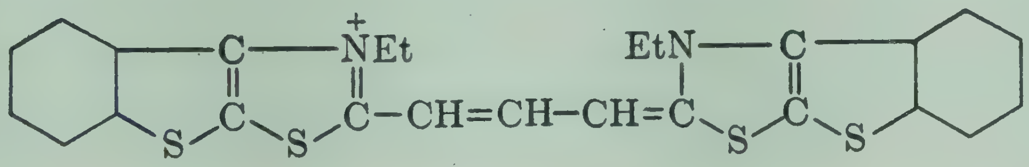
[60] *BIOS* **1433.**
[61] IG, DRP 744,019.
[62] IG, BP 506,720.
[63] Anish and Hensley, CP 441,072.

(I), which extend the sensitivity of silver halide photographic emulsions.[64] Cyanine dyes with recurring nuclei, which are fast to diffusion in emulsion layers, are prepared by using methylene bromide, glycerol dibromohydrin, etc., for linking the nitrogen atoms of the usual heterocyclic intermediates and then proceeding with cyanine dye condensations.[64] *N*-aryloxy-, arylthio and arylseleno-alkyl cyanine dyes have been described.[64a] 4-Furyl and 4-benzofuryl-2-methylthiazoles yield sensitizers.[65] The thiazoline derivative (II) sensitizes to 5250A with a maximum at 4950A; it is prepared by condensing thioacetanilide with ethylene dibromide, converting into the perchlorate, and condensing with ethyl orthoformate.[66] The thiazolothionaphthene derivative (III) extends the sensitivity to 7000A with maxima at 5400A and 6000A.[67]



(II)



(III)

Hamer and her collaborators have described a series of thiazinocyanines.[68] Some unsymmetrical carbocyanines containing the phenyl-substituted oxadiazole nucleus are green sensitizers.[69] Cyanine dyes which contain at the end of the methine chain a 1,2,4-oxadiazole nucleus and an electronegative group can be used for dyeing fabrics.[69a] Heimbach and GAFC have described cyanine dyes (e.g. IV) derived from 1,3,4-triazaindolizine.[70]

[64] Wilson and du Pont, USP 2,393,351; 2,425,772–4; 2,465,774; Brooker and Eastman Kodak, USP 2,461,137; BP 610,064; Gevaert Photo-Producten, FP 930,514.

[64a] Anish and General Aniline and Film, USP 2,504,615–7; BP 631,124.

[65] du Pont, BP 571,077. See also Knott, Hamer, and Rathbone, USP 2,481,673.

[66] Brooker and Eastman Kodak, USP 2,441,558.

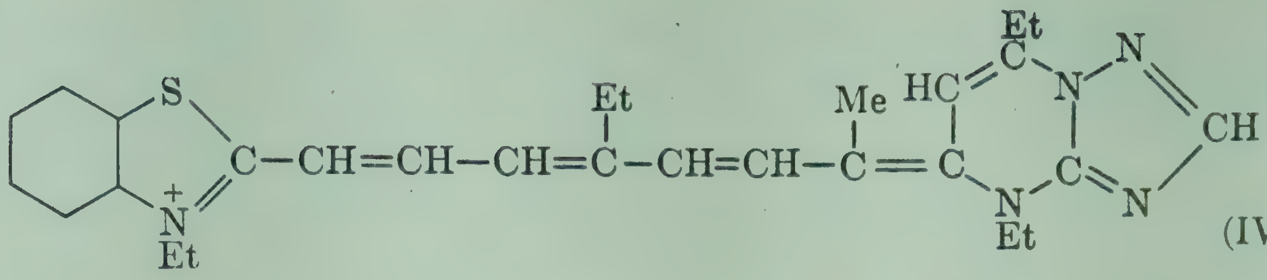
[67] Middleton, Dawson, and du Pont, USP 2,424,483.

[68] *JCS* 222 (**1945**); and earlier papers.

[69] Bauer, Wilmanns, and General Aniline and Film, USP 2,312,068.

[69a] Gevaert Photo-Producten, BP 626,470.

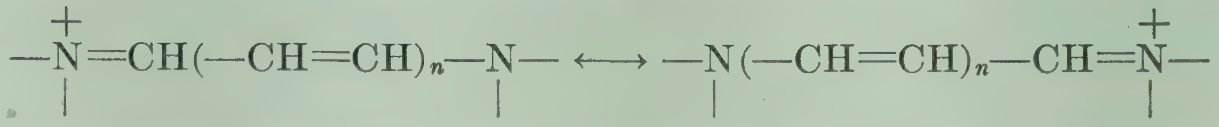
[70] USP 2,443,136. For further examples of miscellaneous cyanine dyes, see BP 627,521; 631,848; USP 2,495,260; 2,464,785; 2,466,523; 2,474,426; 2,481,674.



(IV)

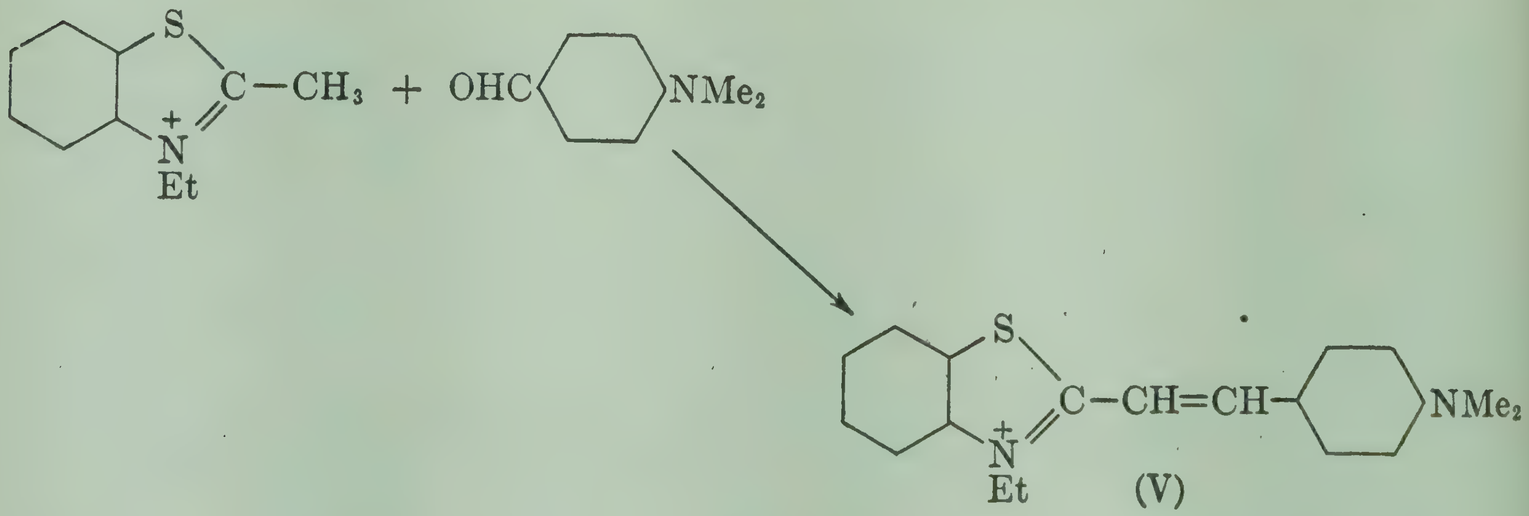
HEMICYANINES

The cyanines may be regarded as part of a wider class of polymethine dyes, defined as ammonium salts containing a polymethine chain $=CH(-CH=CH)_n-$, terminating at either end with a nitrogen atom, so that the cation is a resonance hybrid of the limiting structures (A) and (B). In the cyanines, both the nitrogen atoms are part of ring systems,



$$\text{(A)}\quad -\overset{+}{N}=CH(-CH=CH)_n-N- \longleftrightarrow -N(-CH=CH)_n-CH=\overset{+}{N}-\quad\text{(B)}$$

but it is obvious that there can be varied types of polymethine dyes in which one or both the nitrogen atoms may be extranuclear, and a part of the carbon chain may be included in a ring system. Thus, alkylation of the dianilide of glutaconic aldehyde yields $PhN(Me)-CH=CH-CH=CH-CH=\overset{+}{N}(Me)Ph$ which is an early example of a polymethine dye. While König and others have prepared many representatives of the polymethine class, some of the dyes, especially 2-styrylindole derivatives,[71] have recently proved to be technically valuable for dyeing and printing acetate rayon. A few *p*-dialkylaminostyryl dyes, such as (V), have also been shown to have considerable sensitizing action; they are readily prepared by condensing a heterocyclic compound having a reactive methyl group with a *p*-dialkylaminobenzaldehyde in presence of piperidine.[72] Simple hemicyanine dyes can be prepared by treating a



(V)

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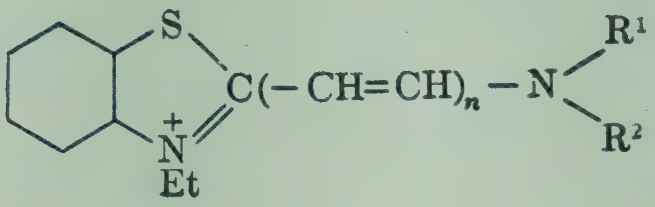
[71] Cf. Eistert and Kochendoerfer, USP 2,350,393.

[72] König, *J. prakt. Chem.* (2) **86,** 166 (1912); Mills and Pope, *JCS* **121,** 946 (1922); Smith, *ibid.* **123,** 2288 (1923); Brooker *et al.*, *JACS* **67,** 1875 (1945); Picus and Spoerri, *ibid.* **70,** 3073 (1948). See also Katayanagi, *J. Pharm. Soc. Japan,* **69,** 137 (1949), *et seq.;* Brooker and White, USP 2,494,032.

cyclammonium salt, having a vinyl group in the α- or γ-position, with excess of a primary aromatic amine.[72a] Greenish yellow to orange dyes for cellulose esters with good fastness to light have been prepared from oxindole, e.g., by condensation with *p*-(bis-2-chloroethyl)aminobenzaldehyde.[73] Vinylene series of the type (VI) in which R^1 and R^2 are H,

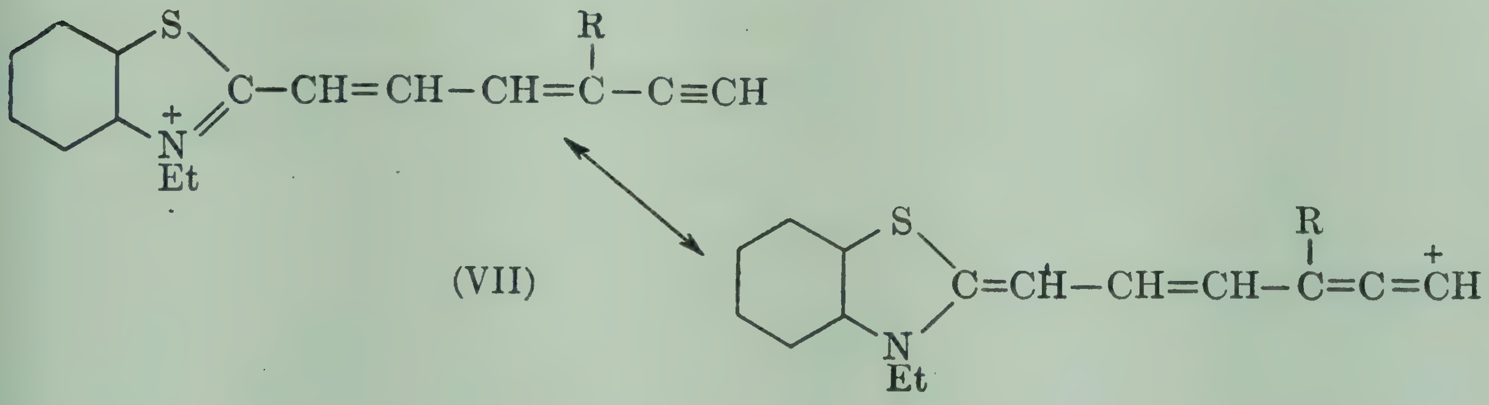


(VI)

alkyl or aryl, or N is part of a heterocyclic nucleus (e.g. piperidine) have also been synthesized.[41, 74] Styryl dyes containing two or more styryl groups can be prepared from such intermediates as 1,4-bis-(*p*-formylphenyl)piperazine.[74a]

Pyrylium salts such as 4-(*p*-dimethylaminostyryl)-7-hydroxy-2-phenylbenzopyrylium chloride, prepared by condensing *p*-dimethylaminobenzaldehyde with 7-hydroxy-4-methyl-2-phenylbenzopyrylium chloride, can be used as filter or antihalation dyes in photographic materials.[74b]

Sensitizing dyes (e.g. VII) of a new and very interesting type are obtained by reacting a pent-2-en-4-yn-1-al (HC≡C—CR=CH—CHO), e.g. the 3-methyl compound, or an aldehydic functional derivative, with



(VII)

2-methylbenzothiazole ethiodide, 2,3,3-trimethylindolenine ethiodide, or similar cyanine dye component.[75]

The Astrazons (IG) are a series of brilliant water-soluble dyes for cellulose acetate,[76] belonging mainly to the polymethine class.[77] Con-

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[72a] Gevaert Photo-Producten, BP 640,094.

[73] Stammers and ICI, BP 595,571.

[74] White, Keyes, and Eastman Kodak, USP 2,166,736; 2,263,749.

[74a] du Pont, BP 622,223; 622,272–3.

[74b] Thompson, and General Aniline and Film, BP 615,252.

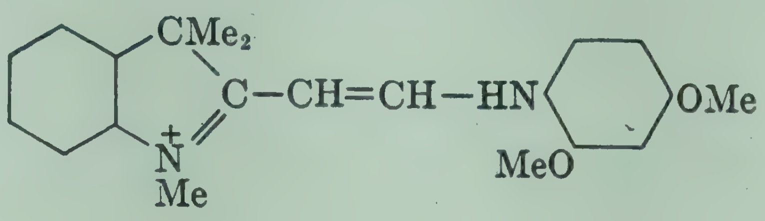
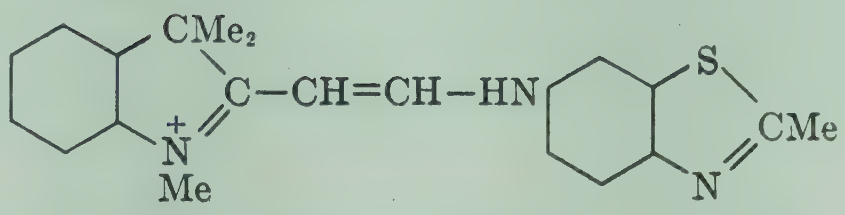
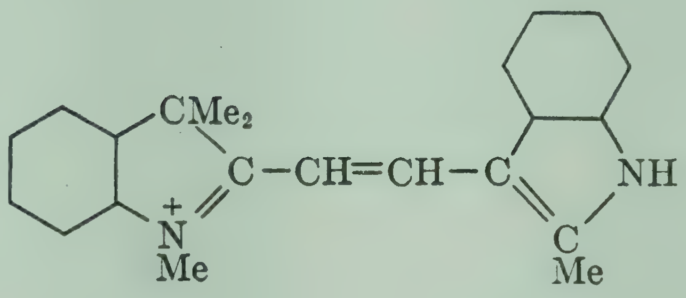
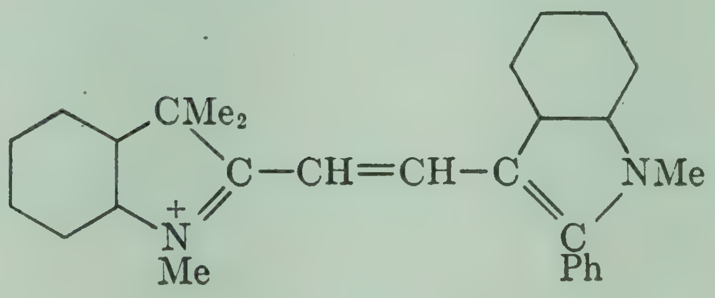
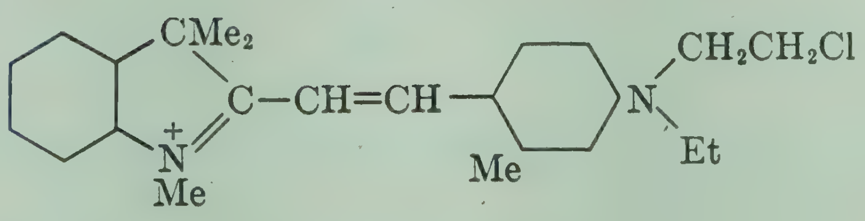
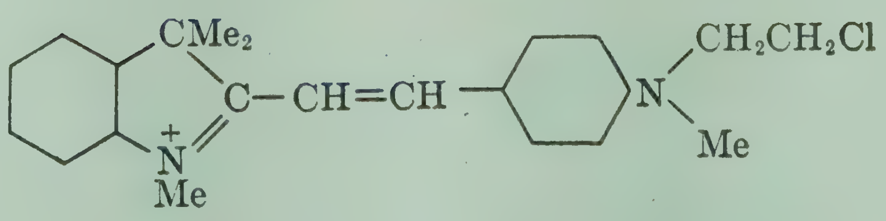
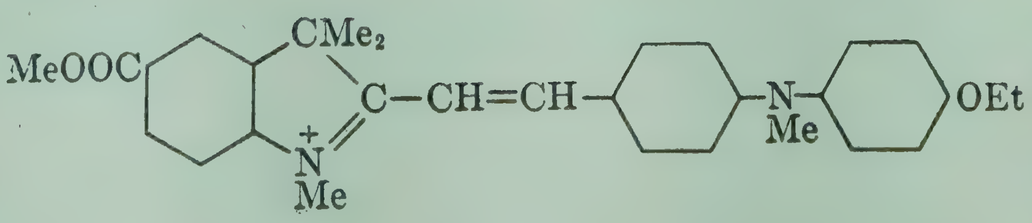
[75] Jones, Reed, and ICI, BP 616,223.

[76] *BIOS* Misc. Report **20**; *BIOS* **1088**.

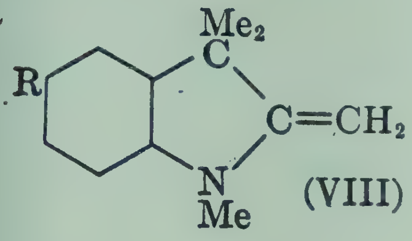
[77] Triphenylmethane dyes of the Astrazon range are mentioned in Chapter XXIII.

TABLE I

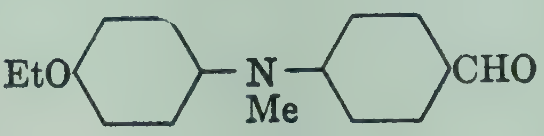
Constitution of the Astrazons of the Polymethine Class

No.	*Astrazon*	*Constitution*	*Components*
1	Yellow 3G		(XI) and 2,4-dimethoxyaniline
2	Yellow 5G		(XI) and 6-amino-2-methylbenzothiazole
3	Orange G		(XI) and 2-methylindole
4	Orange R		(VIII ; R = H) and (XII)
5	Red 6B		(VIII; R = H) and (X ; R^1 = Me, R^2 = Et)
6	Pink FG		(VIII; R = H) and (X ; R^1 = H; R^2 = Me)
7	Violet R		(VIII ; R = COOMe) and (IX).

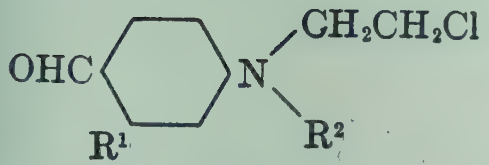
sidering that they are basic dyes related in structure to the light-sensitive cyanines, they are remarkable in their possessing good fastness to light (4–6), besides excellent fastness to washing and sea water. They are recommended especially for printing acetate rayon and mixed fabrics of acetate and viscose; for obtaining the maximum fastness to washing, it is necessary to give the prints, after the usual steaming process, a final treatment with Katanol WL (trichlorobenzylphenol sulfonic acid). The Astrazons are prepared by one of two general methods: (a) the condensation of the indolenine base (VIII) with the appropriate aldehyde (e.g. IX and X) or (b) the condensation of the indolenine ω-aldehyde (XI) with the appropriate amine or 2-methylindole.[78] The aldehyde (XI) is prepared by the direct formylation of the base (VIII) by means of



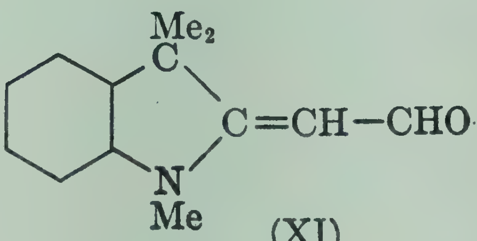
(VIII)



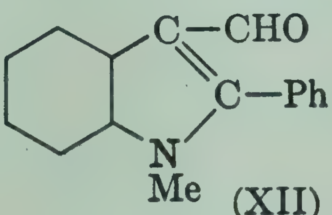
(IX)



(X)



(XI)



(XII)

N-methylformanilide in presence of phosphorus oxychloride or phosgene. 1-Methyl-2-phenylindole-3-aldehyde (XII) and N-methyl-4-ethoxydiphenylamine-4′-aldehyde (IX) are prepared similarly by formylation of 1-methyl-2-phenylindole and N-methyl-4-ethoxydiphenylamine. The polymethine dye is readily obtained by heating the two components in glacial acetic acid solution at about 100°, pouring the reaction mass into water and salting out. The current range of Astrazons, other than the triphenylmethane derivatives, are listed in Table I, and the last column gives the two components which are condensed together to form the dye.

Phosphomolybdotungstic acid lakes of cyanine, carbocyanine, and styryl dyes are bright pigments with excellent fastness to light, stated to be superior to the analogous pigments of the triphenylmethane series (see Chapter XXIII).[79] This is a noteworthy claim since the cyanine dyes are particularly fugitive to light, and with few exceptions, are quite unsuitable for use in dyeing or other coloring purposes.

MEROCYANINES

The name merocyanine (Greek meros = part) was suggested by Hamer for a new class of sensitizing dyes discovered independently by

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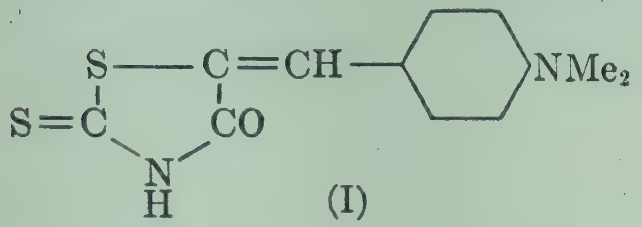
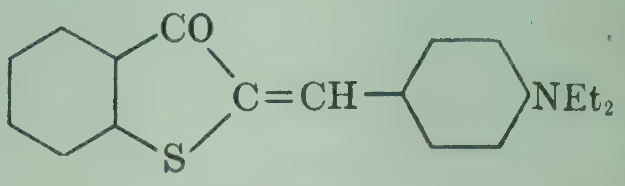
[78] IG, BP 462,238

[79] IG, BP 448,508.

Kendall[80] and Brooker,[81] based on the observation that *p*-dialkylaminobenzylidene derivatives such as 5-*p*-dimethylaminobenzylidenerhodanine

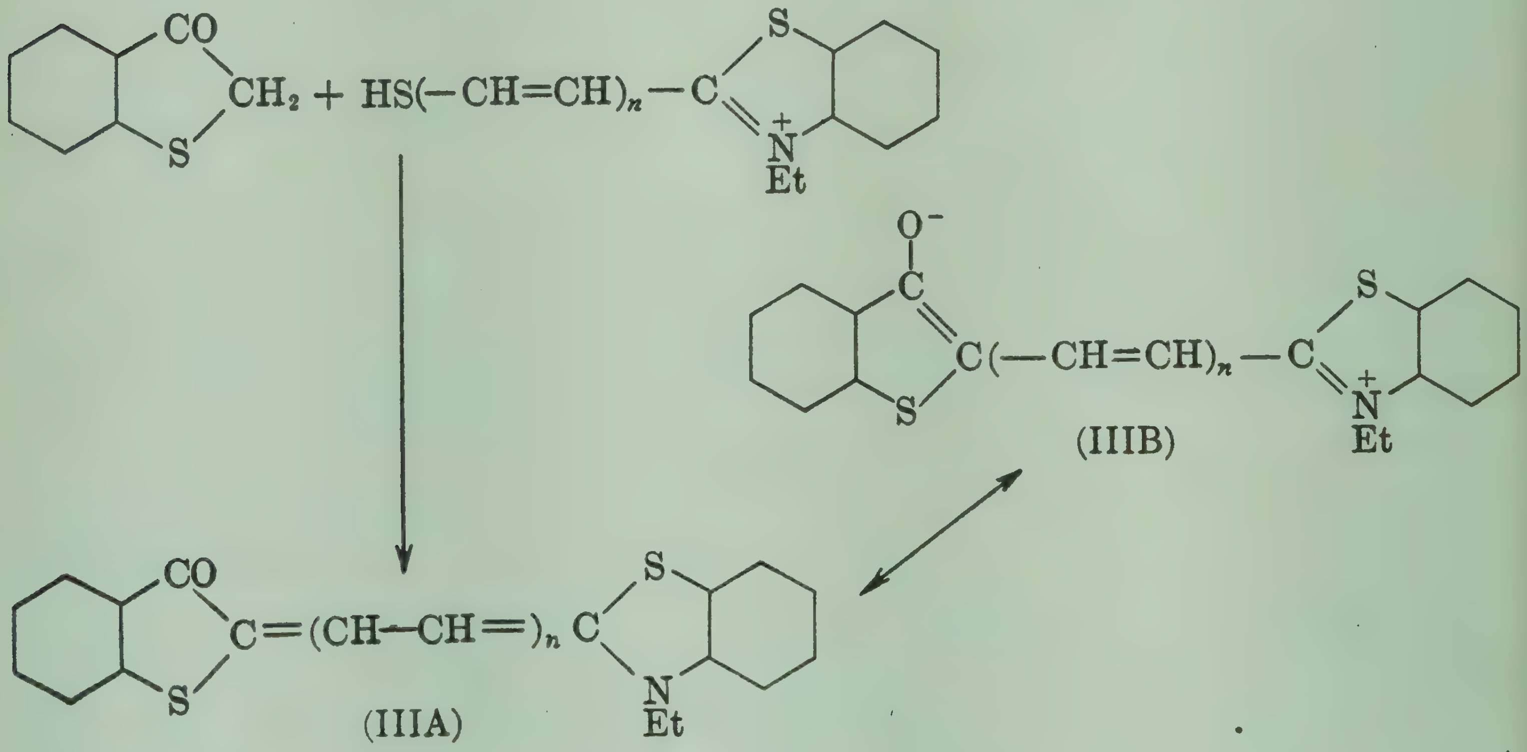


(I)



(II)

(I; Feigl's reagent for silver) and 2-*p*-diethylaminobenzylidenethioindoxyl (II) are good sensitizers. The methods of synthesis are analogous to those described for the true cyanine dyes with the difference that, instead of both the end components being nitrogen-containing heterocyclic compounds, one is a compound with a $-COCH_2-$ group.[81a] Vinylene homologs can be prepared in which $n = 0, 1$, etc. An example is (III), prepared by the condensation of thioindoxyl with the indicated mercapto compound in presence of pyridine or other basic condensing agent. The color of these dyes is associated with resonance between the limiting structures (A) and (B), and they belong therefore to the class of dyes



(IIIB)

(IIIA)

defined by Brooker as possessing the amide system.[2] Numerous merocyanines have been prepared from varied types of compounds containing a $-COCH_2-$ group; open chain compounds, such as acetylacetone and ethyl malonate, and cyclic compounds, such as 1-phenyl-3-methyl-5-pyrazolone and barbituric acid, can be employed. The *N*-alkylrhodanines are of special interest. Unlike the cyanine dyes which are quaternary ammonium salts soluble in general only in water and other polar solvents, the merocyanines are zwitterionic compounds which dissolve in both polar and nonpolar solvents.[81b] Acid merocyanine dyes carrying SO_3H or COOH in the nucleus containing the CO group sensitize less strongly than the corresponding neutral dyes, and leave less stain in the processing of sensitized materials.[81c] Combinations of certain acid merocyanine dyes with selected cyanine dyes produce sensitization in some spectral regions greater than that attained by the acid or basic dyes alone.[82] Basic dyes (e.g. IV) of the merocyanine type for use in dyeing were prepared by IG by condensing the appropriate ω-aldehyde with a rhodanine.[83] The dyes had poor fastness to light.

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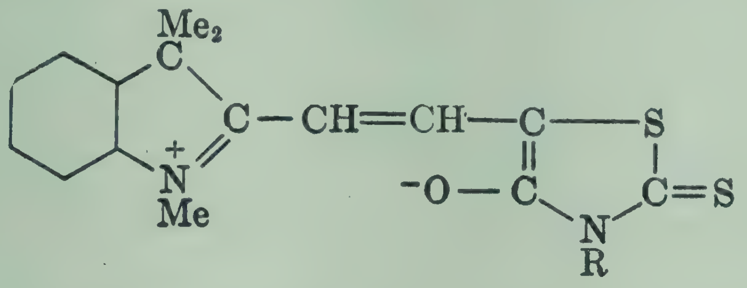
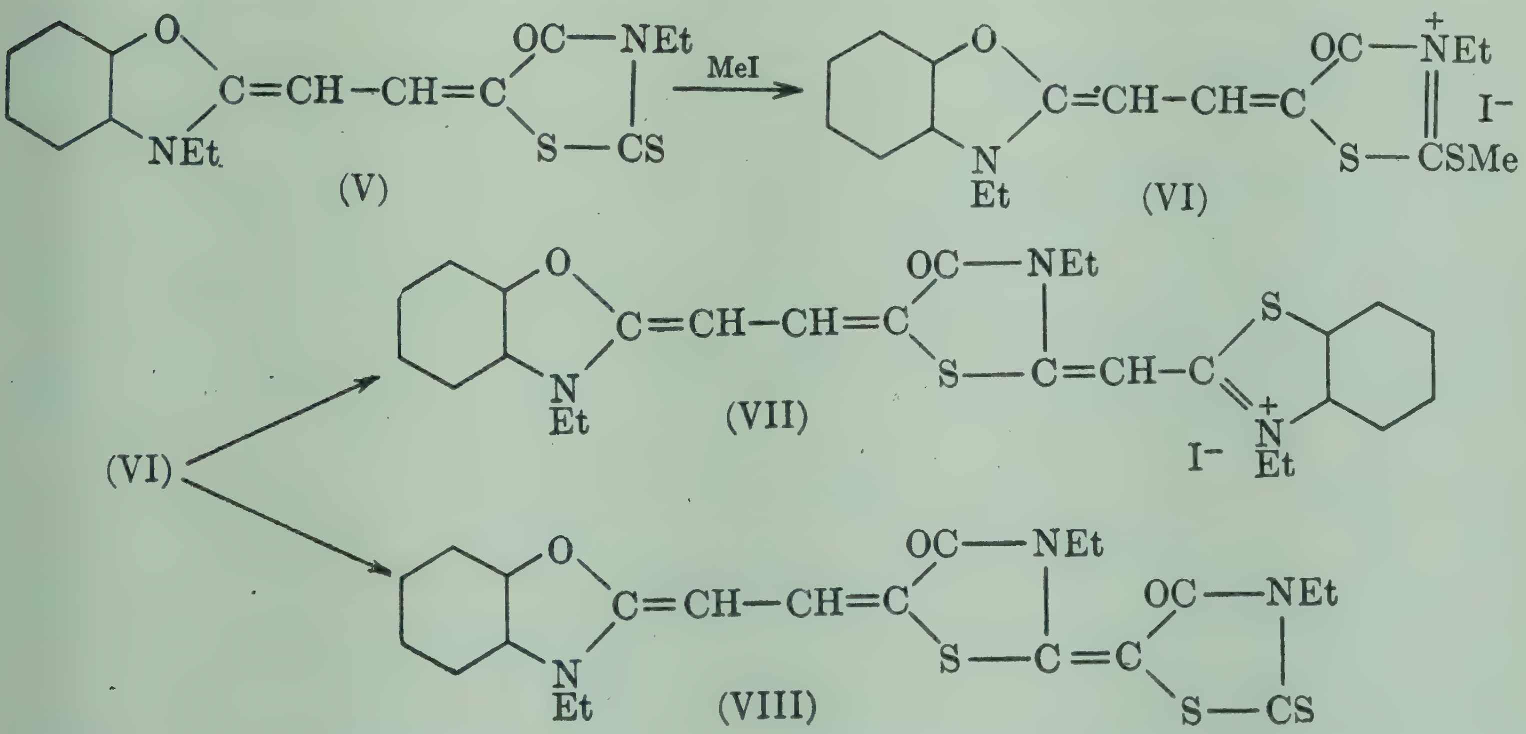
[80] Kendall, BP 426,718; 428,222; 428,359–60; 432,628; 549,201–4; 557,549–50; 624,027; 634,951–2.

[81] Brooker *et al.*, USP, 2,078,233; 2,089,729; 2,153,169; 2,161,331; 2,165,219; 2,165,338; 2,170,803–7; 2,177,401–3; 2,185,182; 2,185,343; 2,186,624; 2,211,762; 2,332,433; BP 606,141; see also Rodd and Watts, USP 2,032,502; Ogata, *Bull. Inst. Phys. Chem. Research Tokyo* **13,** 556 (1934).

[81a] See also van Dormael and Nys, *Bull. soc. chim. belges* **57,** 355 (1948).


(IV)

Trinuclear dyes derived from the merocyanines are technically important photographic sensitizers. It was shown independently by Kendall[84] and Brooker[1, 81] that, like other compounds containing the



[81b] van Dormael has observed that the rhodanine ring in the merocyanine dyes is opened by repeated crystallization from ethanol; *ibid.* **58**, 403 (1949).

[81c] Brooker and White, USP 2,493,747.

[82] Carroll, Brooker, and Spence, USP 2,430,558.

[83] IG, BP 505,839.

[84] BP 487,051; 489,335. See also BP 638,021–4; 638,047.

group —NR—CS—, the merocyanines react with alkyl salts to give alkylmercapto compounds such as (VI). Like the alkylmercapto compounds used for the cyanine syntheses cited earlier, (VI) condenses with 2-methylbenzothiazole ethiodide and similar intermediates to form a new type of complex cyanine dye (e.g. VII). By condensing (VI) with an *N*-alkylrhodanine, dyes such as (VIII) can be prepared. Dyes (VII) and (VIII) are deeper in color than the parent merocyanine (V) (see Fig. 3); but the spectra of the more complex dyes are not more complex, and the light absorption must be associated with the movement of a cationic charge along the length of the molecule as a whole. Unbroken conjugation between the nitrogen atoms of the two outer nuclei in (VII) can be pictured by postulating an amide resonance in the middle ring. Among

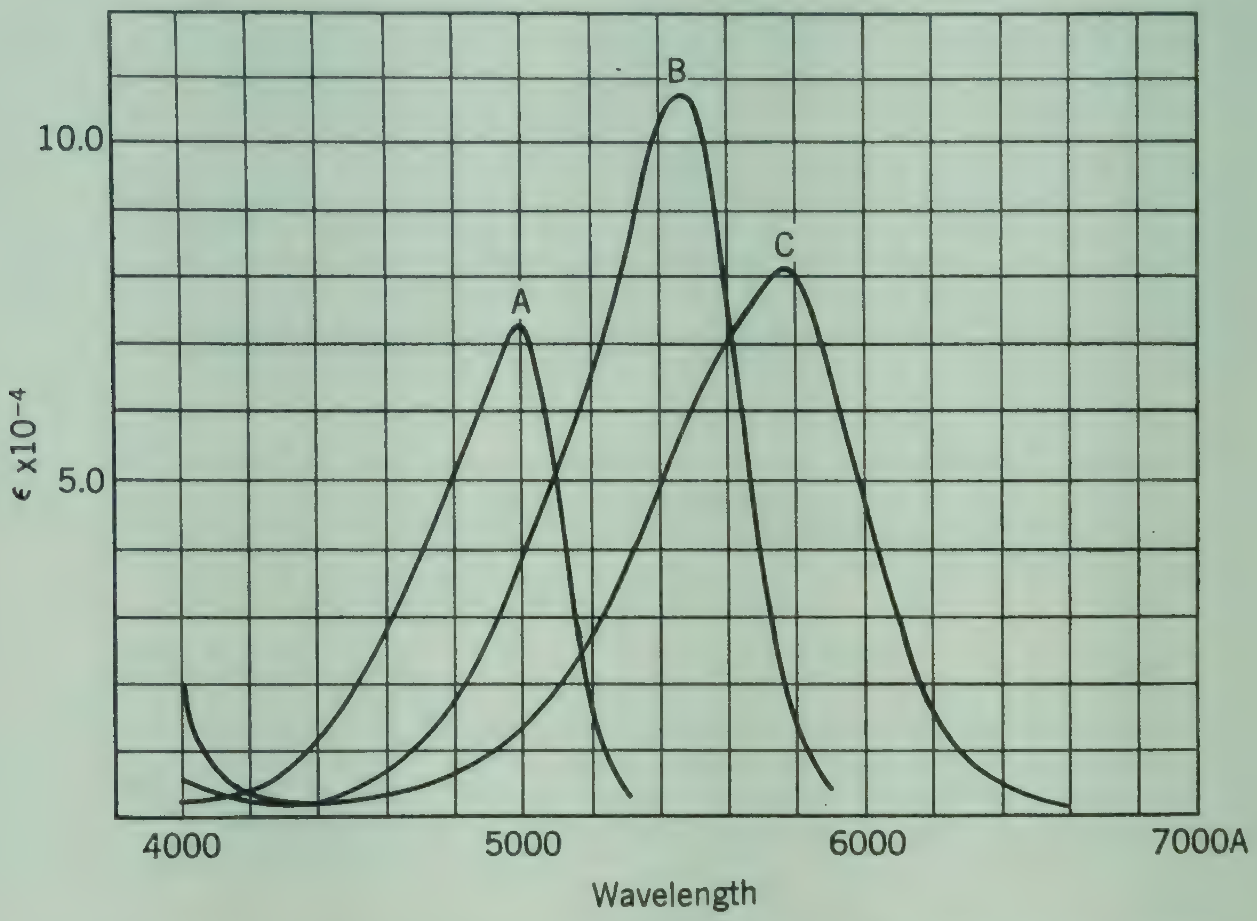
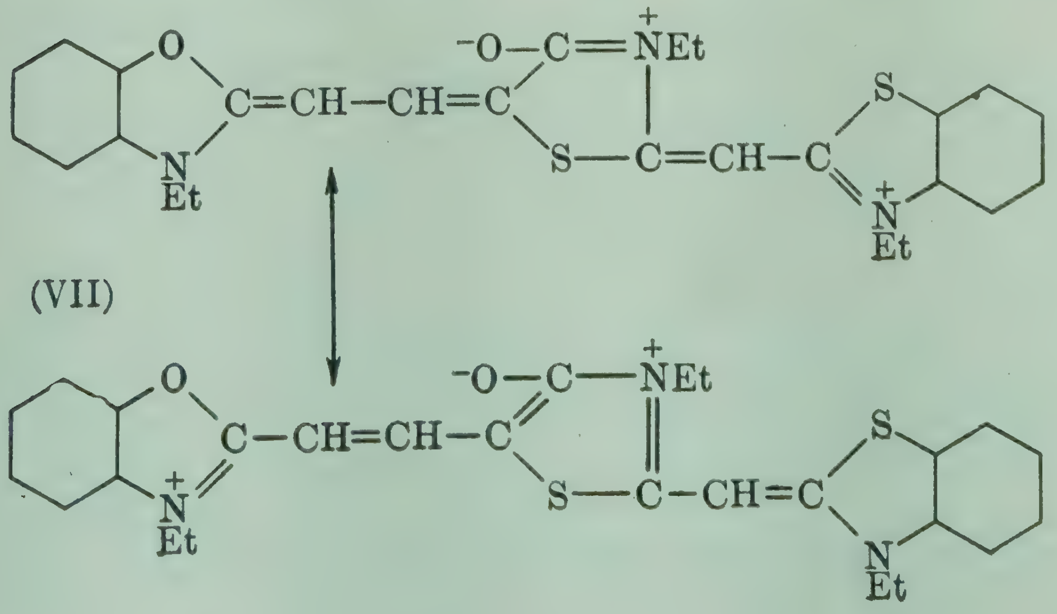
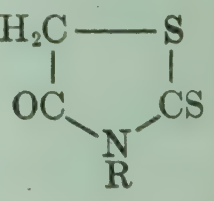


Fig. 3. Absorption spectra in pyridine: A, formula (V); B, (VIII); C, (VII) (Brooker).



(VII)

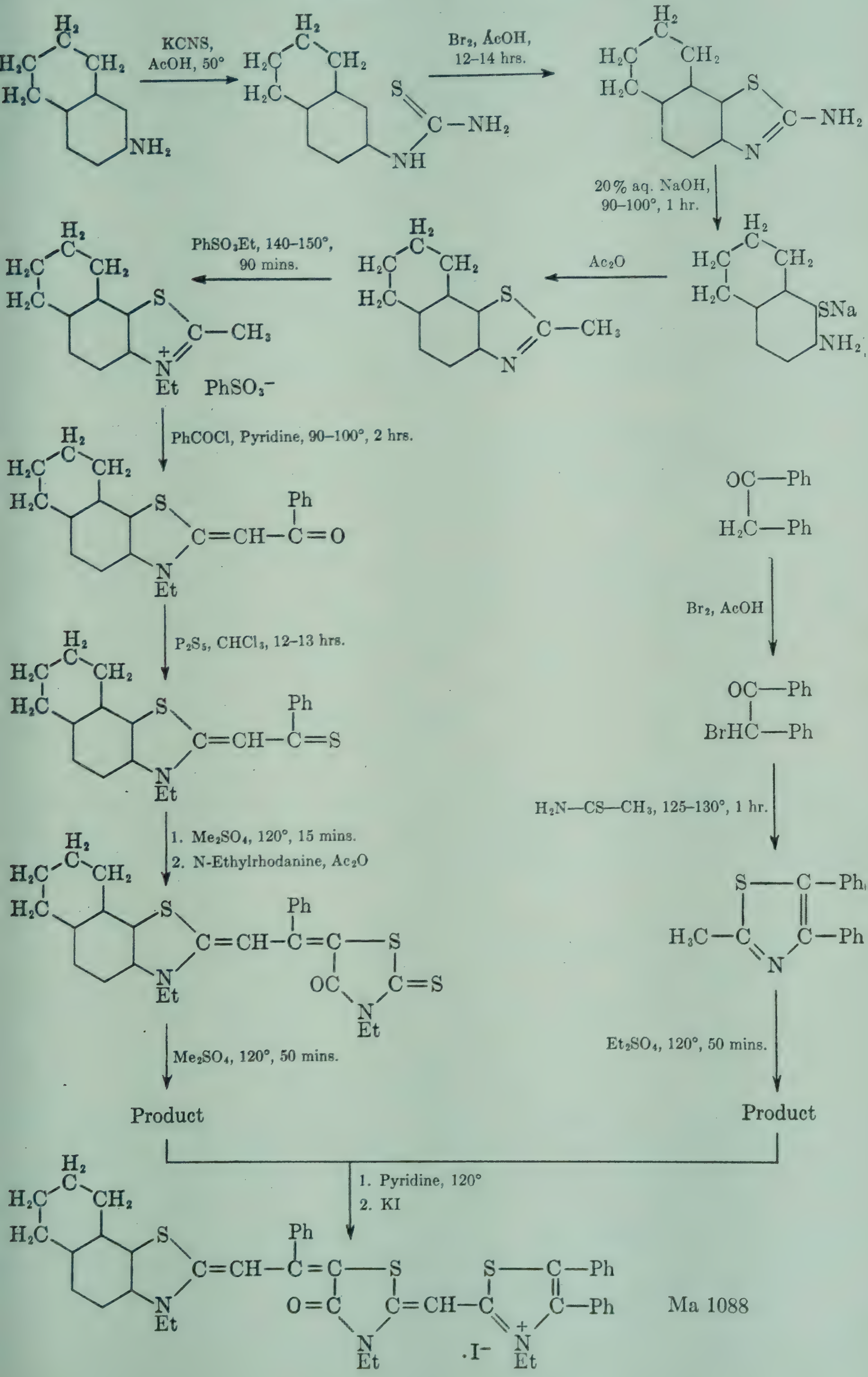


(IX)

R=Et or allyl

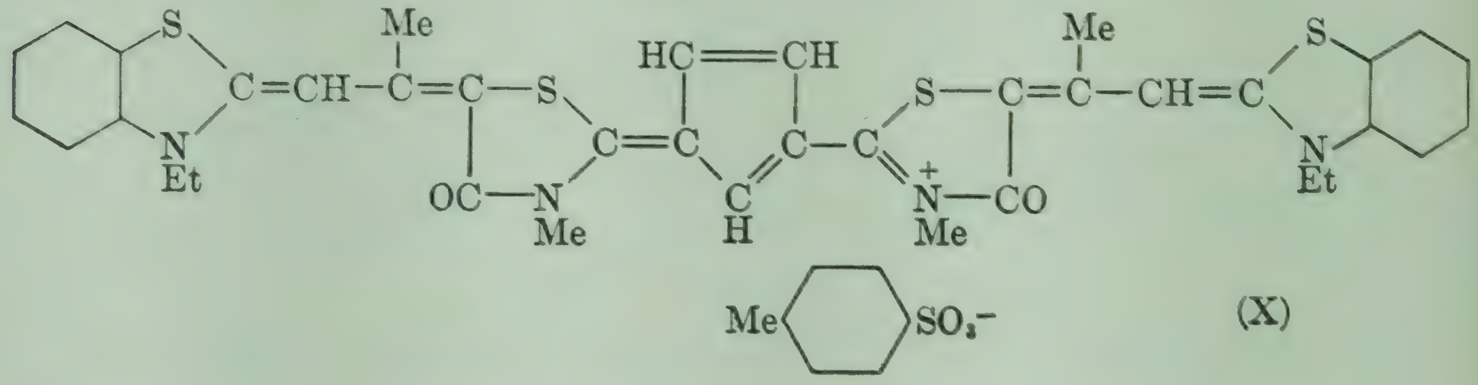
CHART 4

PREPARATION OF MA 1088

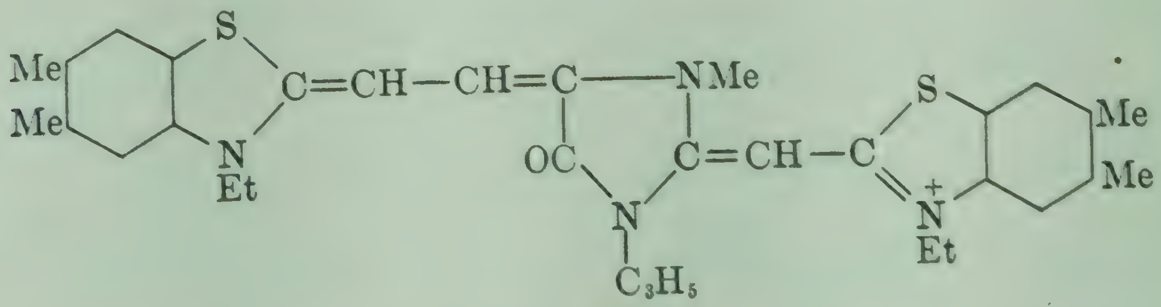

KCNS, AcOH, 50°
Br$_2$, AcOH, 12–14 hrs.
20% aq. NaOH, 90–100°, 1 hr.
Ac$_2$O
PhSO$_3$Et, 140–150°, 90 mins.
PhSO$_3^-$
PhCOCl, Pyridine, 90–100°, 2 hrs.
P$_2$S$_5$, CHCl$_3$, 12–13 hrs.
1. Me$_2$SO$_4$, 120°, 15 mins.
2. N-Ethylrhodanine, Ac$_2$O
Me$_2$SO$_4$, 120°, 50 mins.
Product
Br$_2$, AcOH
H$_2$N—CS—CH$_3$, 125–130°, 1 hr.
Et$_2$SO$_4$, 120°, 50 mins.
Product
1. Pyridine, 120°
2. KI
·I$^-$
Ma 1088

the sensitizing dyes used by IG, there are three examples of cyanine dyes of this type in which the methine chain is interrupted by a thiazolidone ring system. These dyes are derived from *N*-ethyl- or *N*-allylrhodanine (IX) in which the reactive methylene group is condensed with an ω-aldehyde group, and the thiocarbonyl group with the methyl group, in the usual type of heterocyclic intermediate for cyanine dyes. In Ma 1088 (sensitizing max. 5450–5500A) a thiazolidone ring intervenes in the methine chain of a thiazolothiacarbocyanine. The preparation of Ma 1088 (IG) is outlined in Chart 4. Rr 2632 (sensitizing max. 6250–6300A) is of the same type as Ma 1088, and the difference is in the substituents in the benzothiazole components. The preparation of Rr 2632 is outlined in Chart 5. In Rr 1953 (sensitizing maximum 7000–7050A), the synthesis of which is shown in Chart 6, an *N*-allylthiazolidone group intervenes in a trimethine chain between a quinoline and a benzoxazole residue.

Kendall has prepared a large number of merocyanine derivatives such as (X), obtained by appropriate condensations involving *N*-alkylrhodanines.[85] Cyanine dyes (e.g. XI), which are very intense and fast to diffusion, have been prepared by reacting dyes containing the thiohydantoin nucleus with alkyl halides, and condensing the reaction products with nitrogen-containing heterocyclic compounds having a reactive methyl or methylene group.[86] Cyanine and merocyanine dyes have been prepared from 3-ethylmercapto-5,5-dimethyl-2-cyclohexen-1-one (XII); e.g. (XIII) obtained by condensing (XII) first with 2-methyl-



(X)



(XI)

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[85] USP 2,430,295; 2,438,782.

[86] Riester, Wilmanns, Bitterfeld, and General Aniline and Film, USP 2,440,119.

CHART 5

PREPARATION OF RR 2632

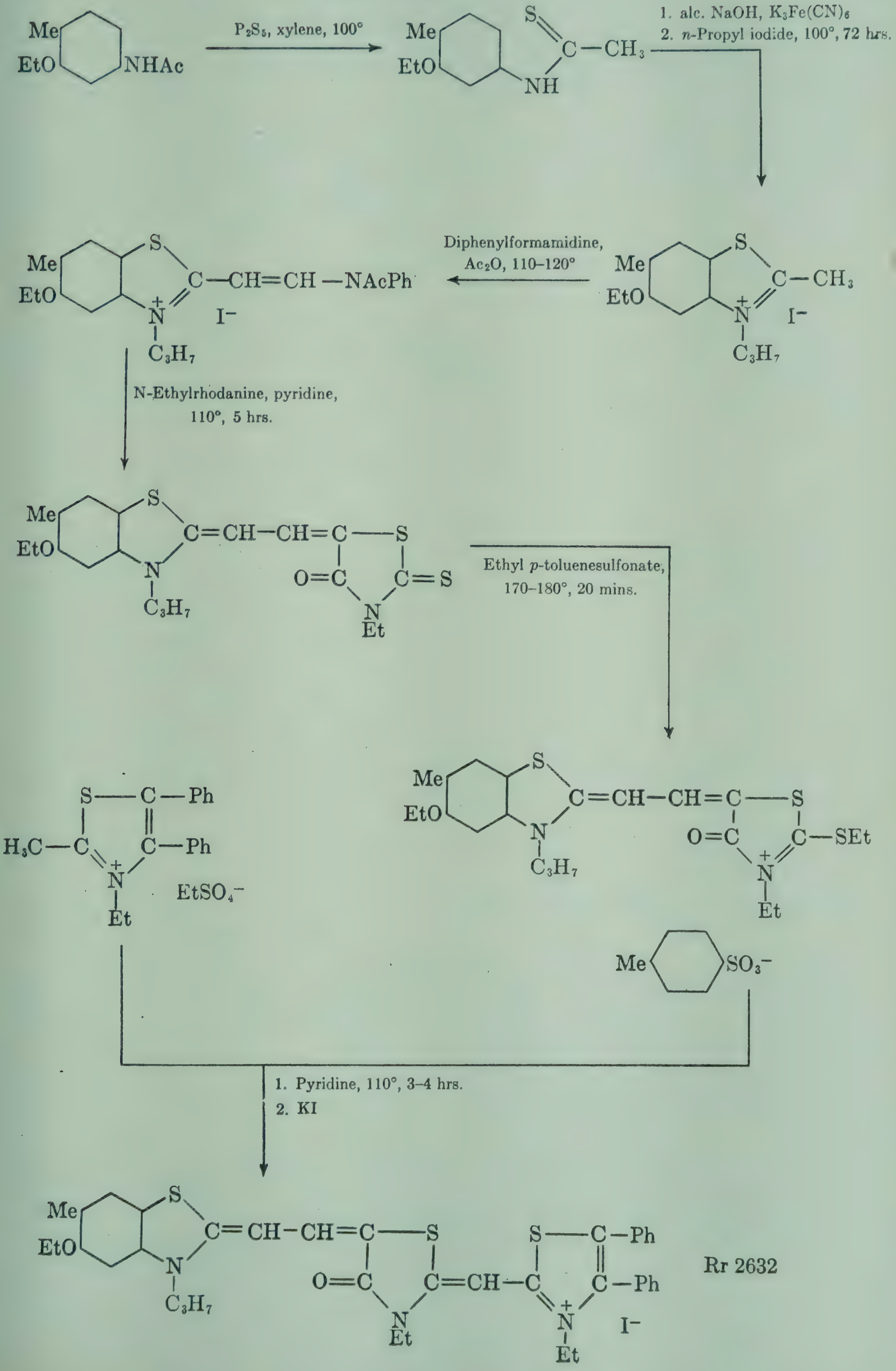
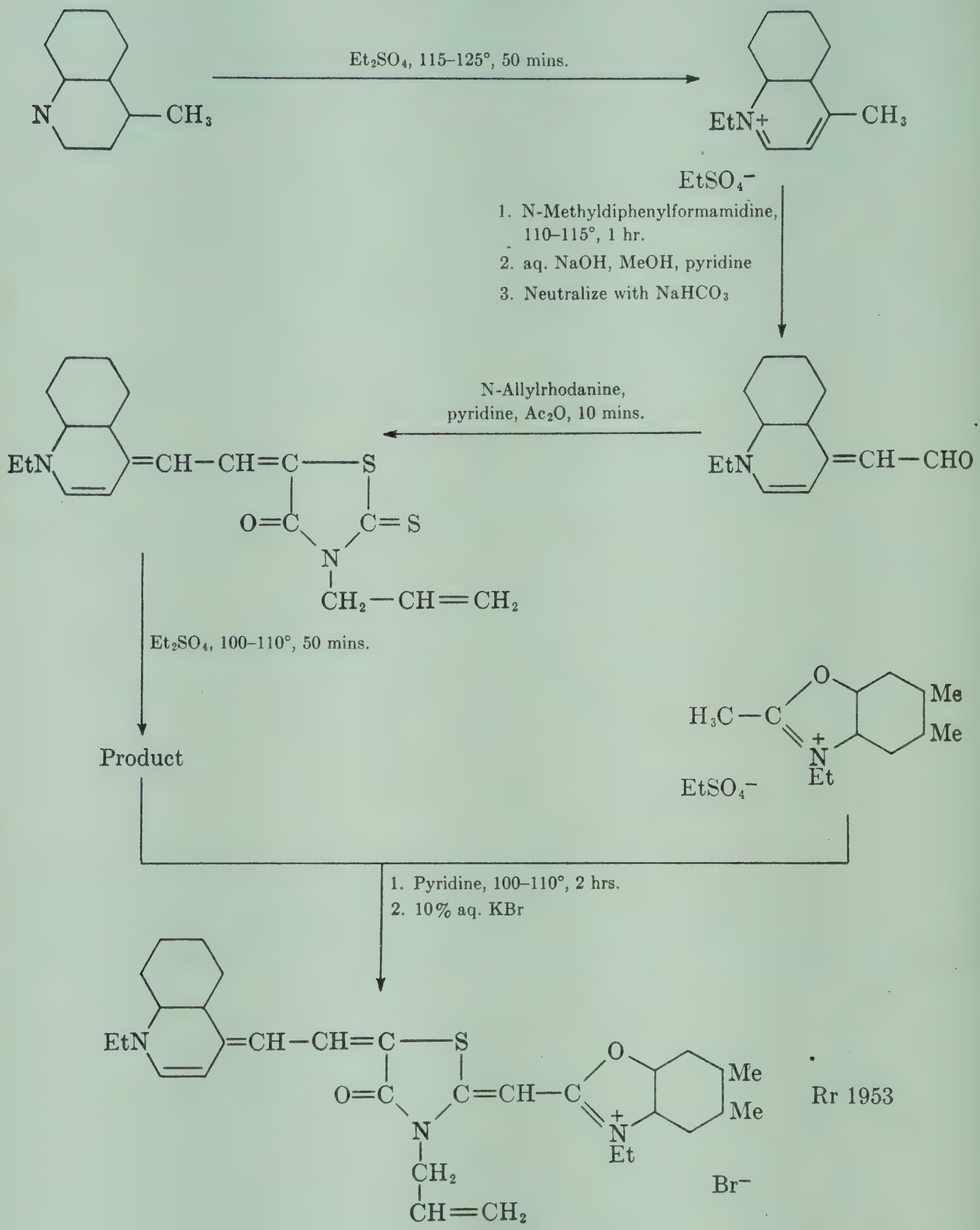
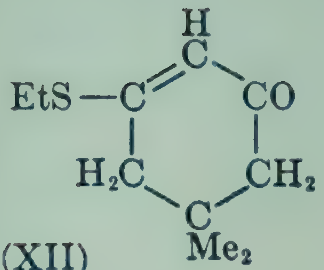

P₂S₅, xylene, 100°
1. alc. NaOH, K₃Fe(CN)₆
2. n-Propyl iodide, 100°, 72 hrs.
Diphenylformamidine, Ac₂O, 110–120°
N-Ethylrhodanine, pyridine, 110°, 5 hrs.
Ethyl p-toluenesulfonate, 170–180°, 20 mins.
1. Pyridine, 110°, 3–4 hrs.
2. KI
Rr 2632

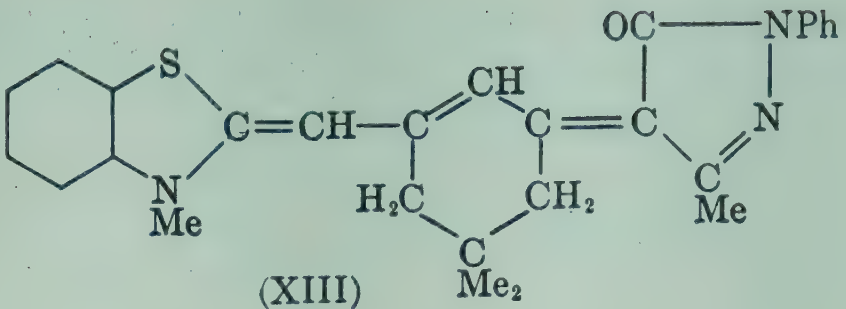
CHART 6

PREPARATION OF RR 1953


N
CH₃
Et₂SO₄, 115–125°, 50 mins.
EtN+
CH₃
EtSO₄⁻
1. N-Methyldiphenylformamidine, 110–115°, 1 hr.
2. aq. NaOH, MeOH, pyridine
3. Neutralize with NaHCO₃
EtN
=CH—CHO
N-Allylrhodanine, pyridine, Ac₂O, 10 mins.
EtN
=CH—CH=C——S
O=C
C=S
N
CH₂—CH=CH₂
Et₂SO₄, 100–110°, 50 mins.
Product
H₃C—C
O
N+
Et
Me
Me
EtSO₄⁻
1. Pyridine, 100–110°, 2 hrs.
2. 10% aq. KBr
EtN
=CH—CH=C——S
O=C
C=CH—C
N
CH₂
CH=CH₂
O
N+
Et
Me
Me
Br⁻
Rr 1953



(XII)

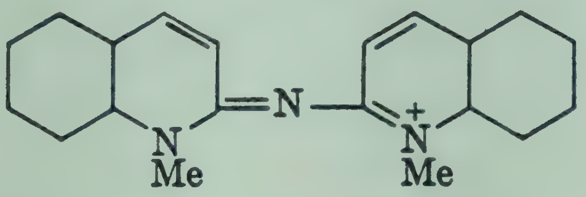


(XIII)

benzothiazole and methyl *p*-toluenesulfonate in presence of acetic anhydride, and then condensing the product with 1-phenyl-3-methyl-5-pyrazolone in pyridine solution.[87]

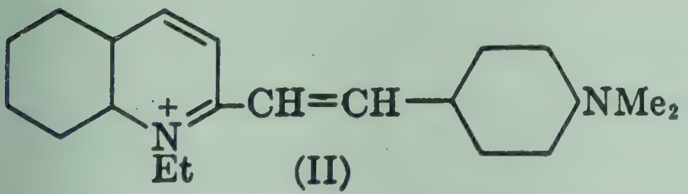
AZACYANINES

Azacyanines are polymethine dyes in which one or more of the methine groups is replaced by a nitrogen atom. An example is (I), prepared by Hamer.[88] The effect of the central nitrogen in this compound

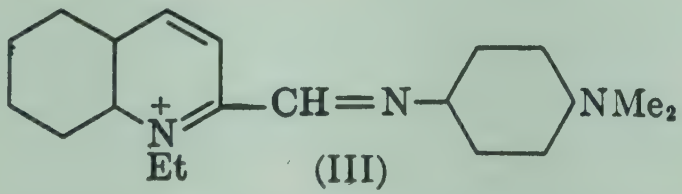


(I)

is to lighten the color relative to the corresponding cyanine with a methine bridge. A method of preparation is to condense a quaternary salt of a nitrogen-containing heterocyclic compound carrying an alkylthiol group with ammonia or a suitable amine.[89] Some azacyanines have proved useful as desensitizers, the function of which is to decrease the sensitivity of photographic films and plates so that a dark room is not necessary for developing them. The interesting relationship between the sensitizing and desensitizing action is shown by the dyes (II) and (III). The styryl dye (II) is a sensitizer, and the anil (III) a desensitizer.



(II)



(III)

Kendall[89] associates the desensitizing activity with the separation of the intermediate nitrogen atom from the terminal nitrogen atom by an even number of carbon atoms in (III). Azacyanines in which this separation is effected by an uneven number of carbon atoms are usually sensitizers. Brooker[1] has explained this position by considering the aza derivatives

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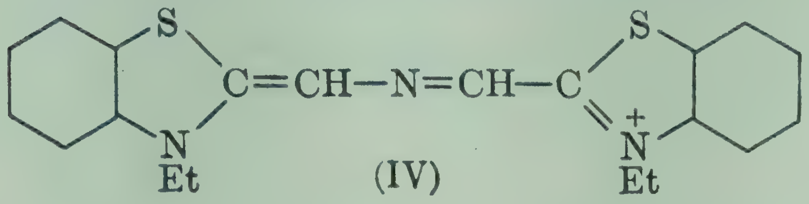
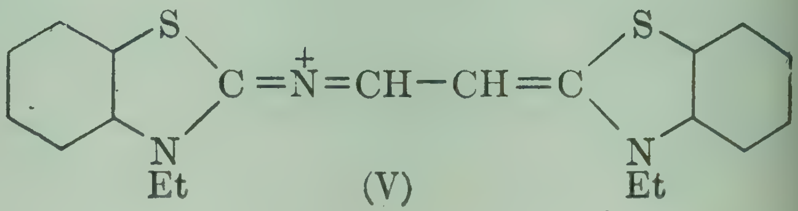
[87] Kendall, Doyle, and Ilford Ltd., BP 595,783–5; 604,217.

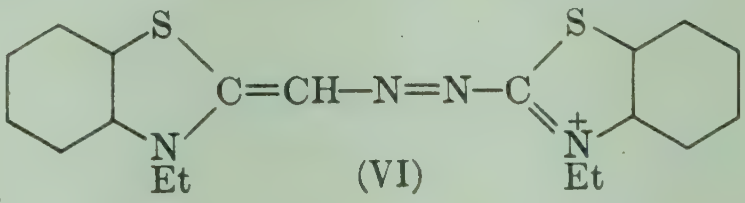
[88] Hamer, *JCS* **125,** 1348 (1924); Fisher and Hamer, *ibid.* 907 (**1937**).

[89] Kendall, BP 447,038; 447,109; 461,668; 544,646. For the synthesis of azadimethine cyanines using 3-nitrosoindoles or 3-aminoindoles, see Mann *et al.*, *JCS* 670 (**1944**); 2903, 2911 (**1949**).

(IV) and (V) of a thiacarbocyanine; (IV) is a strong desensitizer, and further, it has practically no sensitizing properties. The central N is separated from the terminal N atoms by two C atoms on each side, and the central N cannot share the quaternary charge with the terminal N atoms. In (V) on the other hand, the intermediate N is separated from the terminal N atoms by one and three C atoms, and the former can share the cationic charge as indicated; (V) accordingly is less deep in color, but the fragment between the intermediate N and each of the terminal N atoms has the structure of a cyanine dye, so that (V) is a sensitizer. Brooker suggests that Safranine,[90] shown by Lüppo-Cramer to be a desensitizer,[91] owes this property to the fact that, of the four N atoms present in the dye, the cationic charge can be shared only by three. This is also true of Pinakryptol Green,[90] which has been widely used as a desensitizer. Other examples in support of his hypothesis have also been cited by Brooker. The diazacarbocyanine (VI), prepared by condensing the *p*-dimethylaminoanil of 2-aldehydo-*N*-ethylbenzothiazolium perchlorate with *N*-ethyl-2-benzothiazolone hydrazone,[92] is a powerful desensitizer, but also a weak sensitizer for green,[92] because one of the N atoms in the chain makes the compound analogous to (IV) and the other to (V).


(IV)


(V)


(VI)

Under certain conditions of pH and pAg, desensitizers form reversible oxidation-reduction systems, while the strongly sensitizing dyes behave irreversibly.[93] Desensitization by sensitizing dyes has been studied recently by Spence and Carroll.[94] The effectiveness of a given sensitizing dye is the resultant of its spectral absorption, efficiency of transfer of adsorbed energy to the silver halide, and desensitization of the emulsion. Desensitization, measured by the change in sensitivity at 4000A, is an important factor in sensitization, even with the best sensitizing dyes.

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[90] See Chapter XXV.

[91] *Z. angew. Chem* **40,** 1225 (1927).

[92] Fuchs and Grauaug, *Ber.* **61,** 57 (1928). For the synthesis of other diazacarbocyanines see Fisher and Hamer, *JCS* 907 (**1937**).

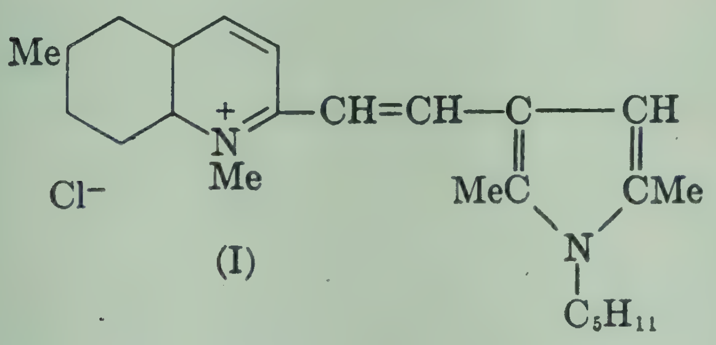
[93] Sheppard, Lambert and Walker, *J. Phys. Chem.* **50,** 210 (1946). An example of simple substitution converting a sensitizer into a desensitizer is 6,6′-dinitrothiacarbocyanine; Kendall, BP 543,993.

Trinuclear azacyanine dyes and azamerocyanine dyes have been described.[94a]

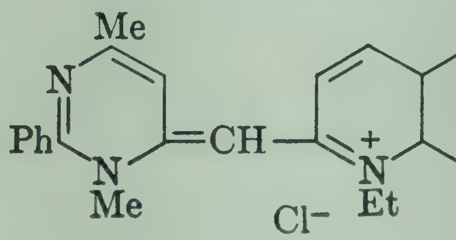
BACTERIOSTATIC AND CHEMOTHERAPEUTIC ACTIVITY OF CYANINE DYES

Cyanine, styryl, and similar dyes appear to have interesting properties as bacteriostatic and chemotherapeutic agents.[95] Brooker has synthesized a long series of new cyanine dyes from this point of view, and has found that many of the cyanine types have pronounced antifilarial and anthelminthic action.[96] Some showed antimalarial activity, but not equal to the well-known antimalarials.

(1-Amyl-2,5-dimethyl-3-pyrrole) (1,6-dimethyl-2-quinoline) dimethinecyanine chloride (I) inhibits the oxidative metabolism of the filarial parasite in concentrations of 6×10^{-6} *M* or less.[96] This cyanine also completely inhibits the growth of *Lactobacillus casei* at $2 \times 10^{-6}M$. In order to determine the nature of the bacterial inhibition, the effect of the cyanines on various cell enzyme systems was studied, but there was no appreciable effect. The cyanine dye (II) is outstanding in its activity against microfilaria in the cotton rat, but it has little or no chemotherapeutic effect against the chief form of human filaria (*Filariasis Bancrofti*).[97] Cyanine dyes such as (II) have been found to be "suitable



(I)



(II)

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[94] *J. Phys. & Colloid Chem.* **52,** 1090 (1948).

[94a] Anish and Clark, USP 2,476,525; Thompson and General Aniline and Film, USP 2,496,899; BP 636,403.

[95] Browning, *Edinburgh. Med. J.* [N.S.] **44,** 497 (1937). See also McKinstry, *J. Am. Pharm. Assoc.* **38,** 146 (1949).

[96] Brooker and Sweet, *Science* **105,** 496 (1947).

[97] Peters, Welch *et al.*, *Science* **105,** 486 (1947); *J. Pharmacol. Exptl. Therap.* **96,** 460 (1949).

for treating roundworm infestations."[97a] The Japanese are said to have made progress with dyes of the neocyanine type as cures for leprosy;[98] but two of the neocyanines claimed by the Japanese have been synthesized by Brooker, and found to be inactive against leprosy and tuberculosis.[99]

[97a] Brooker *et al.*, USP 2,472,565.

[98] Hamer, *Chemistry and Industry* 660 (**1947**).

[99] Brooker, *private communication.*

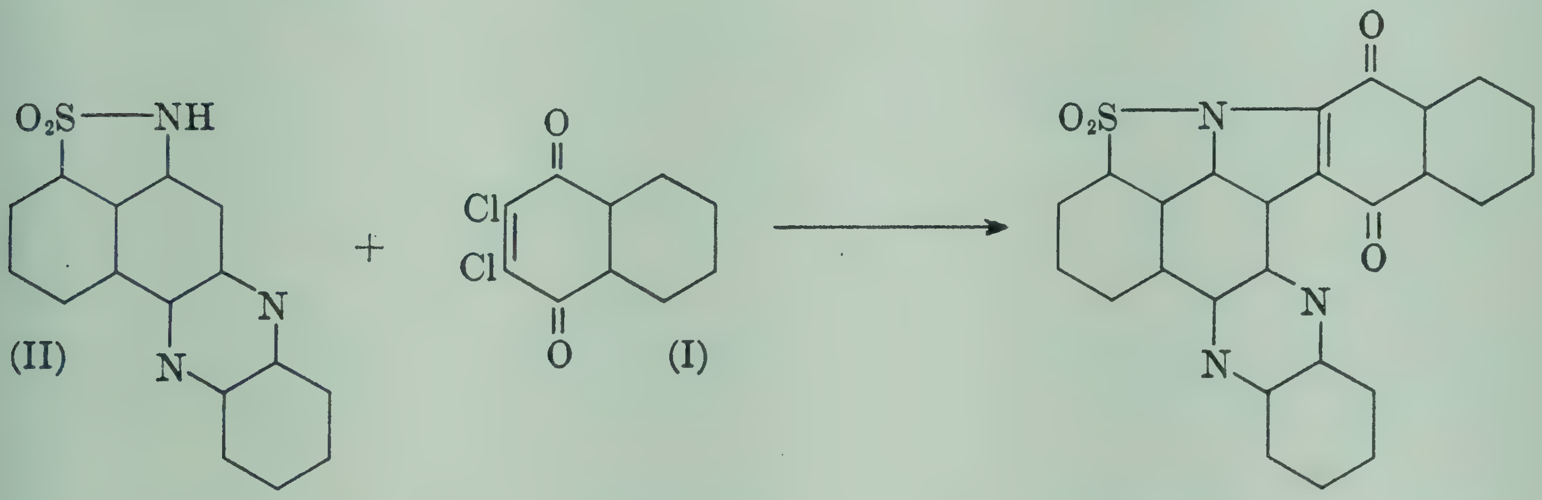
Chapter XXXIX

MISCELLANEOUS DYES

It is convenient to collect together the miscellaneous dyes which do not readily fit into the chemical classification followed in the preceding chapters.

Derivatives of 1,4-Naphthoquinone

Indanthrene Yellow 6GD is a vat dye derived from 1,4-naphthoquinone, and is prepared by condensing 2,3-dichloro-1,4-naphthoquinone (I) with the azine (II) in nitrobenzene solution in presence of sodium acetate. The azine (II) is obtained by nitrosating naphthasultam and heating the nitroso compound with *o*-phenylenediamine in aqueous sodium carbonate solution until no more ammonia is evolved. Indanthrene Yellow 6GD dyes greenish yellow shades with excellent fastness to light and the dye is notable for its lack of cellulose-tendering activity associated with many yellow vat dyes of the anthraquinone series.[1, 1a]



Indanthrene Yellow 6GD

Another naphthoquinone derivative is (III), prepared by condensing 3-halogeno-2-amino-1,4-naphthoquinone with an aromatic dicarboxylic acid and converting into the *bis*-oxazole (III) by heating or into imidazoles by the action of primary amines; the yellow vat dyes are bright in shade and have very good fastness.[2]

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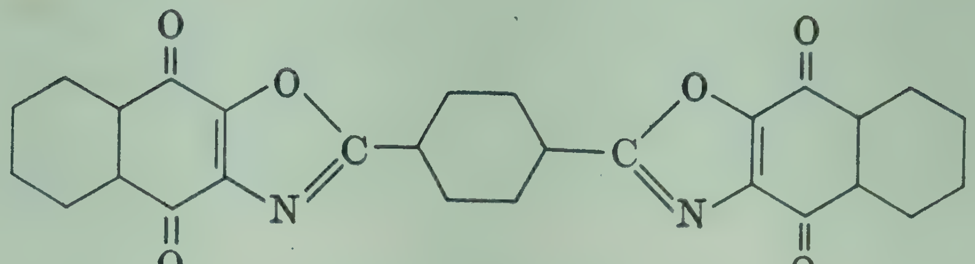
[1] *BIOS* **987.**

[1a] According to Fox, *J. Soc. Dyers Colourists* **65,** 522 (1949), Indanthrene Yellow 6GD, which has very good dyeing properties, is mainly used in fabric printing, and it is an actively tendering dye (see Chapter XL).

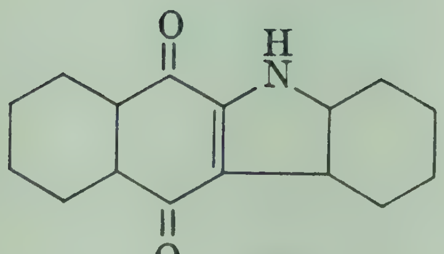
[2] IG, DRP Anm. J. 48,578.



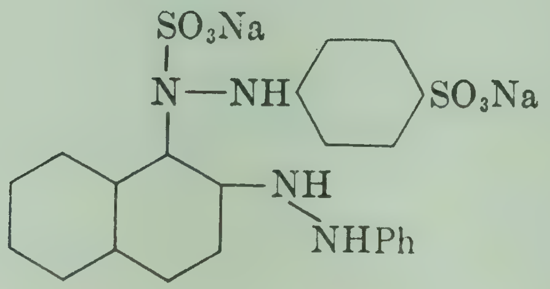
(III)

An interesting vat dye derived from 1,4-naphthoquinone is (IV), obtained by the action of acid on the bisulfite compound (V) of 1-*p*-sulfobenzeneazo-2-phenylhydrazinonaphthalene.[3]

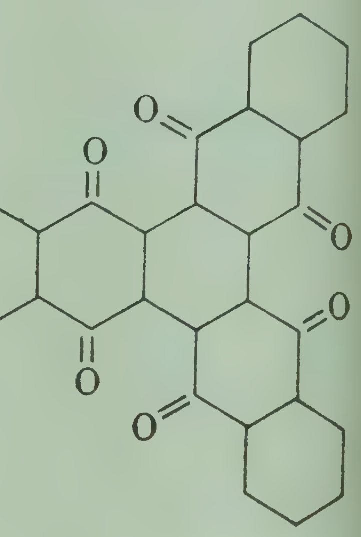
1,4-Naphthoquinone condenses with itself in pyridine solution to give triphthaloylbenzene (VI) in 60% yield. The trichloro derivative gives a yellowish green vat dye on reduction with zinc dust in concentrated sulfuric acid.[4]



(IV)



(V)



(VI)

Derivatives of Naphthalic Acid

Brilliant Sulfoflavine FF (IG; ST II, p. 40) is an acid color for wool. The yellow shades have very poor fastness to light. This interesting dye is a naphthalimide prepared from acenaphthene as shown in Chart 1.[5] Fierz-David[6] mentions Brilliant Sulfoflavine as a dye of similar constitution, in which cyclohexylamine replaces *p*-toluidine. Using 5-aminosalicylic acid for the condensation with (I), the product is Chrome Fast Yellow 8GL or 5GD (IG), a chrome-developed dye for wool.

When (I) is sulfonated to a disulfonic acid and condensed with amines, the products are brilliant yellow dyes fluorescing strongly in ultraviolet light.[6a] Compounds containing suitable *o*- or *peri*-dicarboxyl groups may be dyed on animal fibers and converted into colored insoluble imides on the fiber by treatment with ammonia or amines. Perylene-3,4,9,10-tetracarboxylic acid, for example, may be used to obtain red shades, and other structures have been built up by synthesis from phthalic and naphthalic acid derivatives. Red to blue shades with very good fastness to rubbing, potting and milling are obtained.[7] Yellow dyes for calico printing are obtained by condensing 3- or 4-aminonaphthalic acid or anhydride with aminosalicylic acid; the dyes give reddish yellow chrome prints which resist hydrosulfite.[8]

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[3] Bucherer and Hanusch, *J. prakt. Chem.* (ii) **132,** 274 (1931).

[4] Fierz-David, Blangey, and Krannichfeldt, *Helv. Chim. Acta* **30,** 816 (1947).

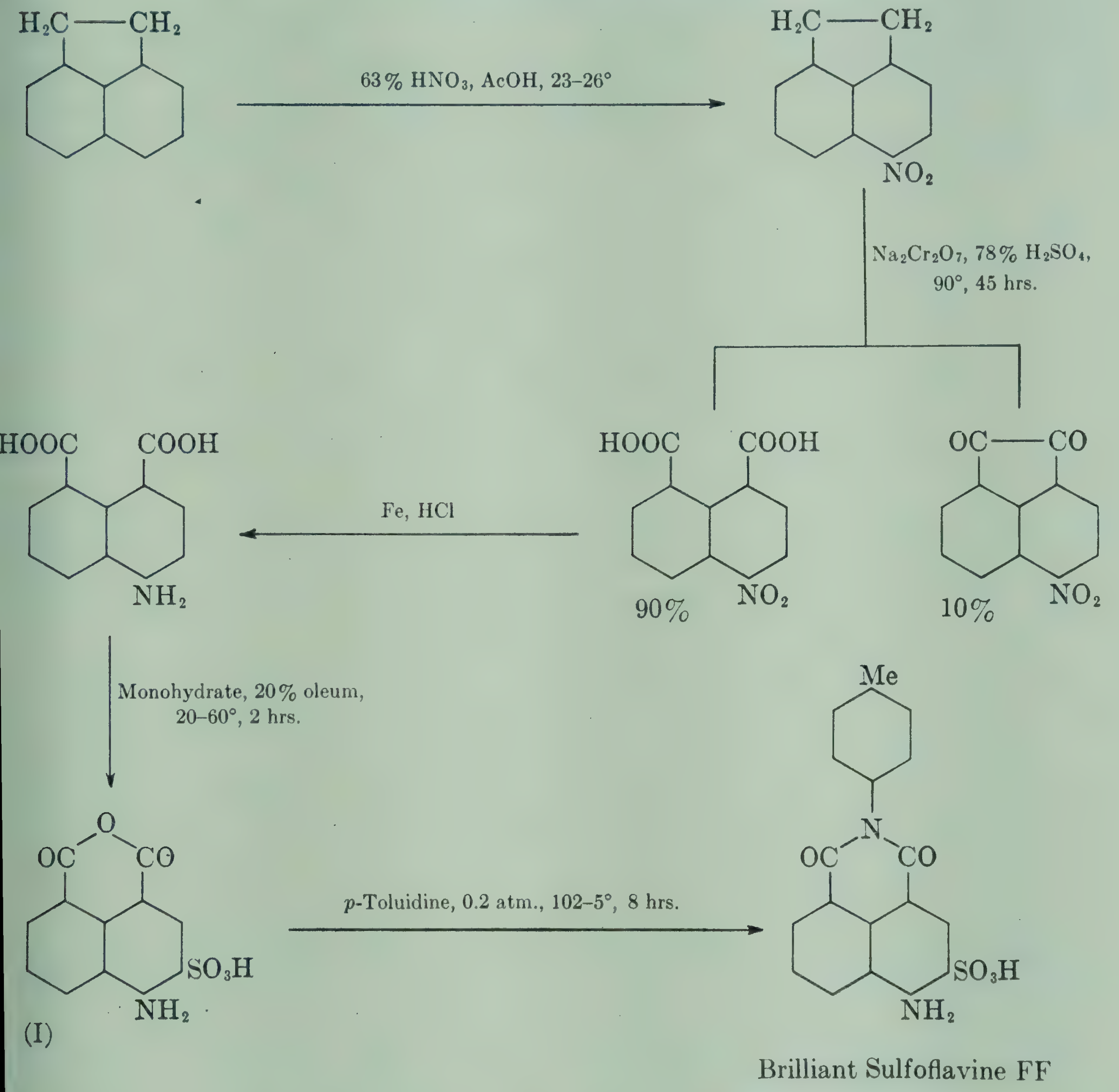
[5] *BIOS* **959.**

[6] Fierz-David, Künstliche Organische Farbstoffe, Ergänzungsband, Springer, Berlin, 1935, p. 10; see also IG, DRP 531,291.

[6a] Scalera, Forster, and American Cyanamid, USP 2,455,095.

CHART 1

PREPARATION OF BRILLIANT SULFOFLAVINE FF


H_2C—CH_2
63% HNO_3, AcOH, 23–26°
H_2C—CH_2
NO_2
$Na_2Cr_2O_7$, 78% H_2SO_4, 90°, 45 hrs.
HOOC COOH
NH_2
Fe, HCl
HOOC COOH
90%
NO_2
OC—CO
10%
NO_2
Monohydrate, 20% oleum, 20–60°, 2 hrs.
O
OC CO
SO_3H
NH_2
(I)
p-Toluidine, 0.2 atm., 102–5°, 8 hrs.
Me
N
OC CO
SO_3H
NH_2
Brilliant Sulfoflavine FF

Vat dyes have been prepared from naphthalene peri-di- and tetracarboxylic acids which are similar in their dyeing and fastness properties to the anthraquinone vat dyes. Fusion of naphthalimide (II) with

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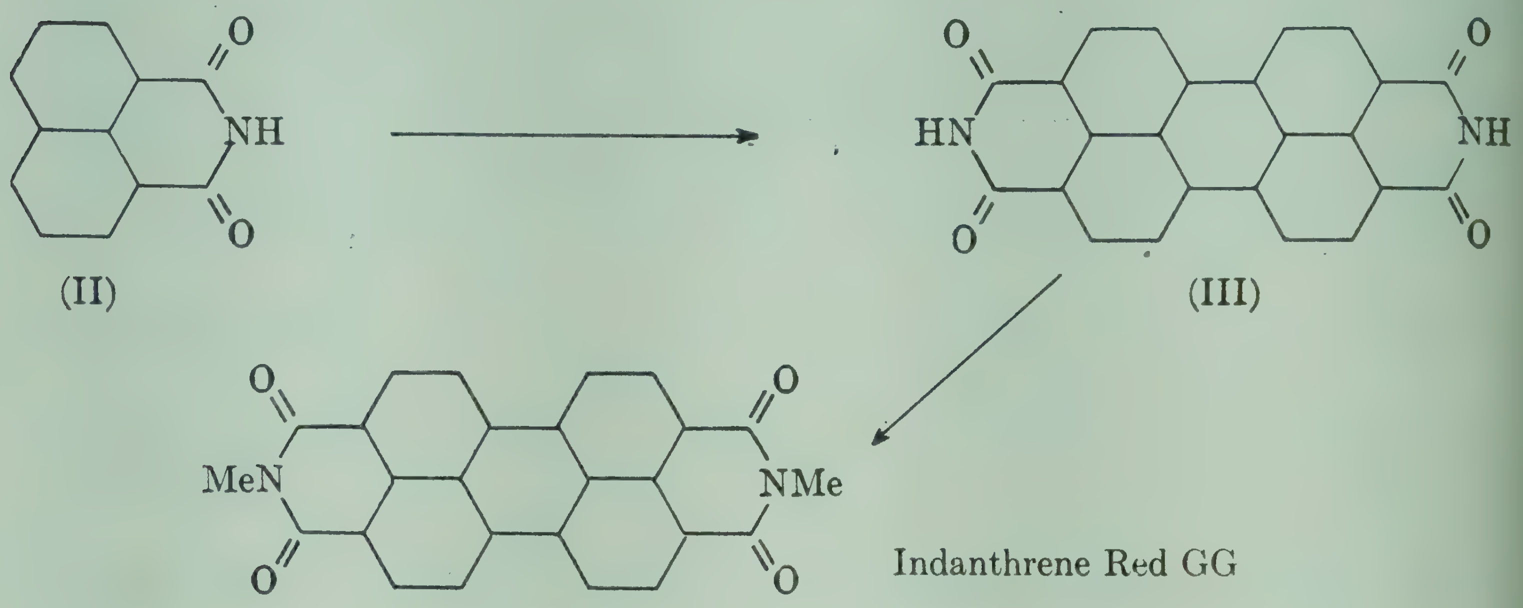
Haddock, Lodge, Lumsden, and ICI, BP 429,681.

Durand and Huguenin, BP 384,901.

caustic potash gives the diimide (III) of perylene-3,4,9,10-tetracarboxylic acid; the *N*,*N*-dimethyl derivative, readily obtained by methylation of (III), is Indanthrene Red GG (Caledon Red 2G) (Cardos and Lüttringhaus, 1914). Besides its being a perylene derivative made from a naphthalene intermediate, the dye is interesting because of its structural difference from the anthraquinone vat dyes. The behavior of this cyclic imide as a vat dye, in comparison with other perylene derivatives such as the dibenzanthrones, merits investigation. The strawberry shades (from a violet vat) have high fastness to light (6–7) and to chlorine (4), but only moderate fastness to alkali boil (2–3).



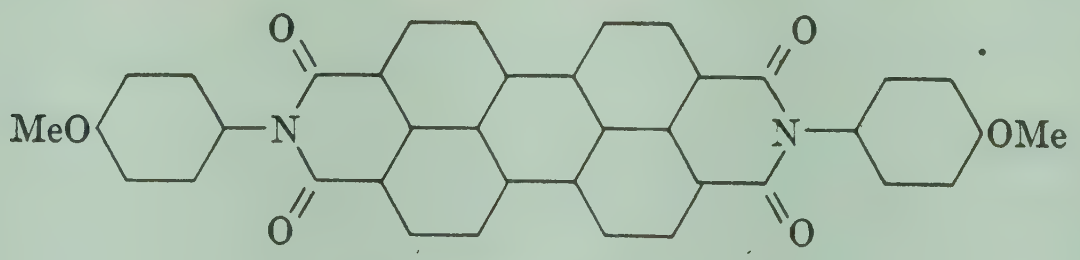
(II)

(III)

Indanthrene Red GG

Aceanthrene Green (Kardos, 1913; CI 1158), a vat dye prepared by the alkali fusion of the imide of anthracene-1,9-dicarboxylic acid, is obsolete; its constitution is not known with certainty and it has the interesting property of dyeing cotton a violet red shade, which changes to an emerald green "by washing in the air," apparently by oxidation beyond the stage of the parent dye.

Heating perylene-3,4,9,10-tetracarboxylic acid with *p*-anisidine, the product is Indanthrene Scarlet R,[9] which has better fastness than Red GG both to chlorine (5) and to alkali boil (3–4), but slightly lower light fastness (5–6). The *p*-chloroaniline analog is Algol Scarlet B. New yellow to red vat dyes have been obtained by condensing naphthalene-



Indanthrene Scarlet R

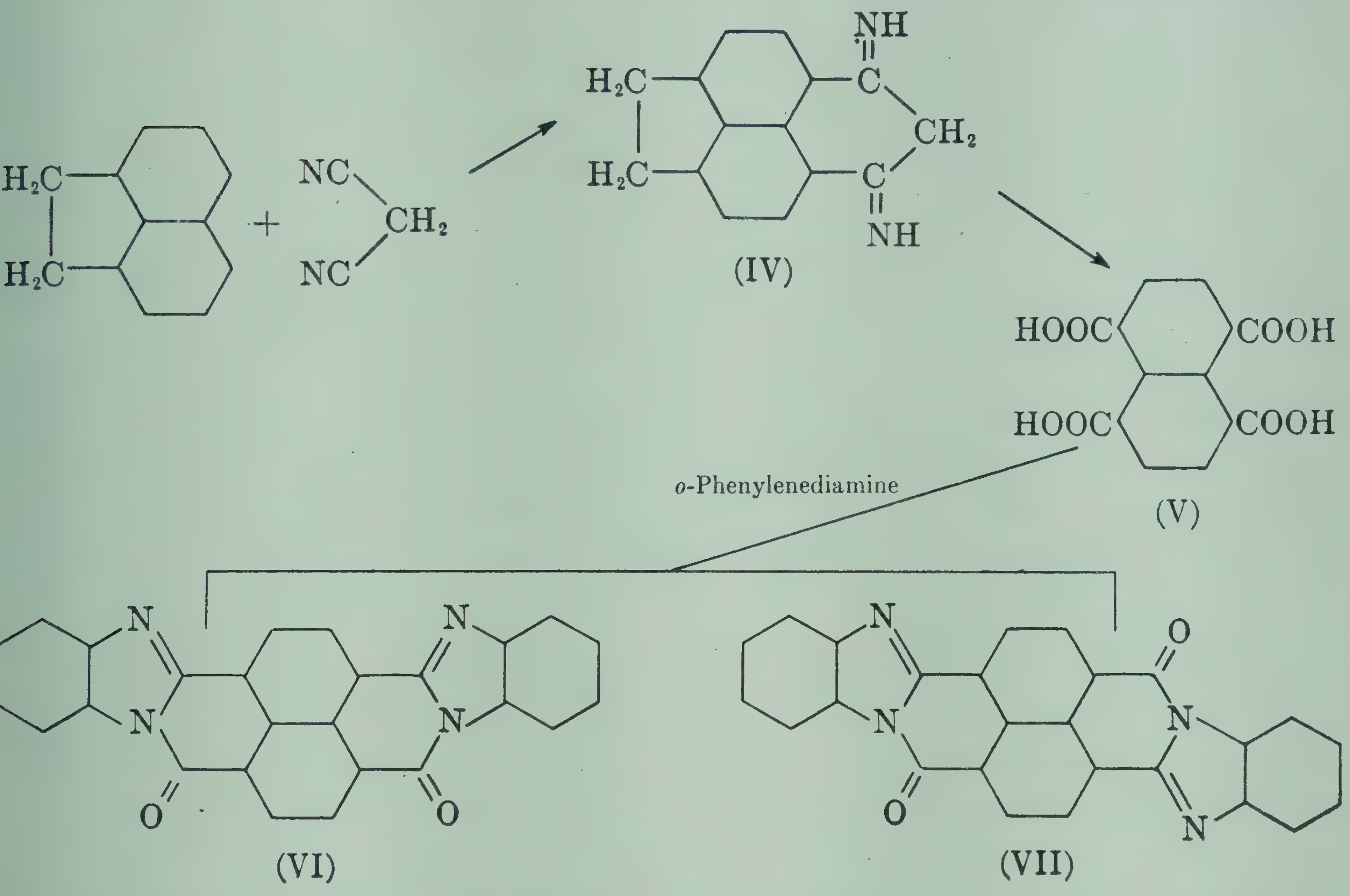
[9] Microfilm FD 2537/46 Frame No. 982.

and perylene-tetracarboxylic acids with *m*-aminobenzoic acid and using the resultant imides to acylate aminoanthraquinones.[10]

Indanthrene Scarlet GG (Eckert and Greune, 1924) and Brilliant Orange GR (1931) are important dyes,[11] which have the additional interest of being made from acenaphthene which otherwise has a very limited use as a raw material for dyes. The condensation of acenaphthene with malononitrile[12] in chlorobenzene solution in presence of aluminum chloride, adding the reactants at 20° and, when the vigorous reaction has subsided, heating finally to 125–130°, gives the diketimide (IV). Oxidation of (IV) by means of sodium chlorate and hydrochloric acid at 40–60° gives naphthalene tetracarboxylic acid (V).[13, 14] Other methods of obtaining naphthalene-1,4,5,8-tetracarboxylic acid are to condense acenaphthene with carbamyl or alkylcarbamyl chloride to give

CHART 2

Preparation of Indanthrene Scarlet GG and Brilliant Orange GR



[10] Haddock and ICI, BP 416,425.

[11] *FIAT* **1313** II gives full details of the IG process.

[12] Malononitrile is prepared by the interaction of cyanoacetamide and phosphorus pentachloride in chlorobenzene. The temperature is raised gradually from 20–70° during several hours, chlorobenzene being simultaneously distilled off under reduced pressure. To the residual malononitrile, hydroquinone is added to prevent polymerization, and the nitrile is purified by distillation at about 4 mm. pressure.

[3] IG, BP 359,201; 362,906; 363,044; 364,116.

[4] For further details see *FIAT* **1298.**

acenaphthene-5,6-dicarboxylic diamides; the reaction can also be applied to fluorene, stilbene, chrysene, pyrene, and similar hydrocarbons.[15] Indanthrene Scarlet GG is obtained by heating the tetraacid (V) (200 kg.) and *o*-phenylenediamine (179) in glacial acetic acid (1350) at 120° in an autoclave for 6–7 hours, cooling to 90°, and filtering off the product. The reaction can take two courses, leading to *cis*- and *trans*-compounds (VI and VII),[16] and Indanthrene Scarlet GG is a mixture of the two. Indanthrene Brilliant Orange GR is the *trans*-compound (VII), separated in a yield of 59% from the mixture by treatment with twice its weight of potassium hydroxide in alcohol (10 parts) at 75° for one hour; a potash addition product of the *trans*-compound separates, which is filtered off, re-treated with alcoholic potash, filtered, washed with alcoholic potash, and hydrolyzed with water. Both the dyes have good all-round fastness (light 6–7; chlorine 5; alkali boil 3–4), and Indanthrene Brilliant Orange GR is the brightest of the oranges among the anthraquinone vat dyes. The residual dye (VI) in the alcoholic filtrate is recovered by distilling off the solvent and acidifying, and is marketed as Indanthrene Bordeaux RR, which dyes a brighter and redder bordeaux shade than Indanthrene Bordeaux B, with good light fastness (6), wash fastness (4) and excellent fastness to chlorine (5). Separation can also be effected by means of sulfuric acid.[17] Vat dyes of the heterocyclic imide and imidazole type can be produced in very finely divided state by slurrying with sulfuric acid to form the insoluble sulfate and then hydrolyzing the sulfate.[17a]

Indanthrene Printing Brown B is an analog of Indanthrene Scarlet GG in which *o*-phenylenediamine is replaced by its 4-ethoxy derivative; this constitution has been assigned by Rowe[18] to Indanthrene Red Brown 5RF which has also been stated to be a carbazole derivative.[19] Indanthrene Printing Brown 5R is similar in constitution to Indanthrene Scarlet GG, 4-chloro-*o*-phenylenediamine being used for the condensation with naphthalene tetracarboxylic acid.[19]

Two variations of the *o*-phenylenediamine method for the preparation of these imidazole dyes have been described. Naphthalene-1,4,5,8-tetracarboxylic acid is condensed with an *o*-aminoazo compound; the products are then treated with a reducing agent, so that fission of the azo group and cyclization to the imidazole both take place.[20] Alternatively, the acid is condensed with *o*-diamines which are substituted in one or both amino groups; the normal imidazole dyes are formed, the substituent (alkyl, acyl or urea groups) being split off during the reaction.[21]

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[15] IG, BP 456,070.

[16] Their absorption spectra have been studied by Gratsche, *Prom. Org. Khim.* **6**, 620 (1939).

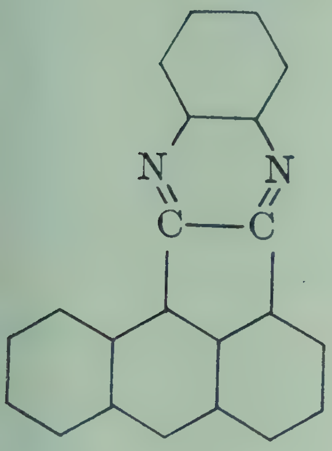
[17] See also IG, BP 403,862; 434,815.

[17a] Cullinan, Lytle, and American Cyanamid, USP 2,473,015.

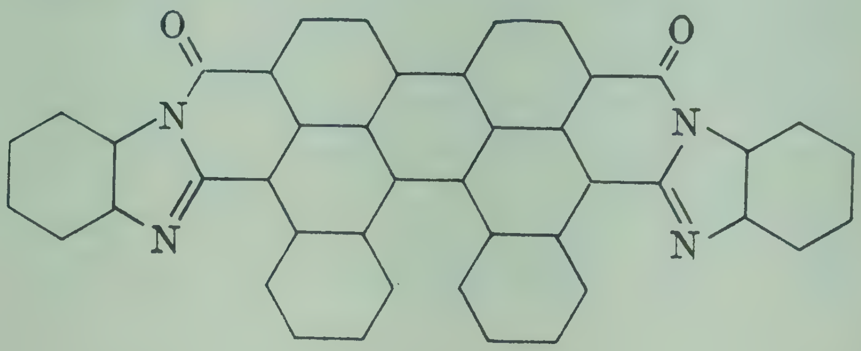
[18] The Development of the Chemistry of Commercial Synthetic Dyes, Institute of Chemistry, London, 1938.

[19] *BIOS* **1493**.

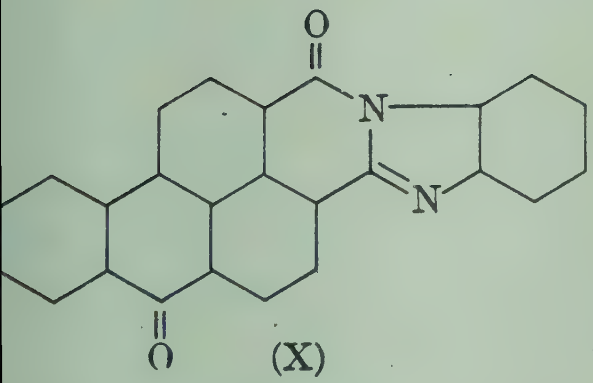
The range of imidazole vat dyes from *peri*-tetracarboxylic acids has been extended, following the preparation of anthracene-1,4,9,10- or 1,5,9,10-tetracarboxylic acid. This product, which may be a mixture of the two isomerides, yields dark blue vat dyes on condensation with *o*-diamines.[22] The imidazoles from perylene-3,4,9,10-tetracarboxylic acid dianhydride and *o*-phenylenediamine dye in navy blue shades.[23] Green vat dyes are produced by the alcoholic potash fusion of the quinoxalines obtained by condensing aceanthrenequinone with *o*- and *αβ*-diamines.[24] The starting products (VIII) contain no keto groups, but it is possible[25] that these dyes are imidazole analogs (e.g. IX) of Aceanthrene Green.



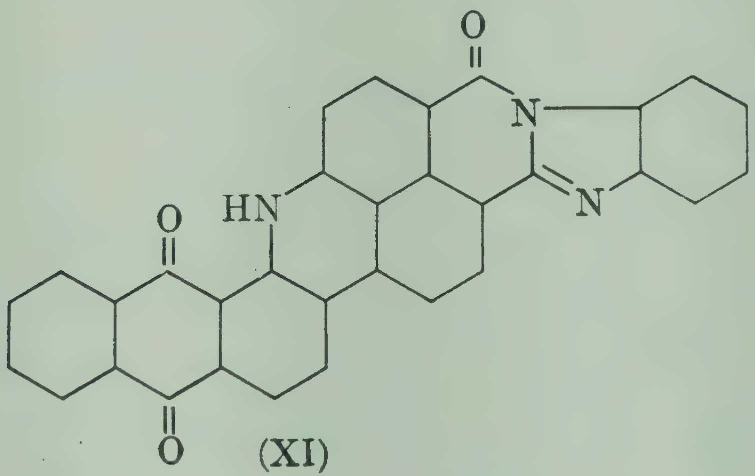
(VIII)



(IX)



(X)



(XI)

Dyes have been prepared which are derived from naphthalene- or other dicarboxylic acids and which contain only one imidazole ring, in contrast with the Indanthrene Scarlet GG type which contains two such systems. Examples are (X) and (XI); (X) is an orange vat dye, while (XI) dyes green from a red-violet vat.[26] Two forms, *cis*- and *trans*-, are possible as for Indanthrene Scarlet GG, but the stereochemistry of the products, which will be particularly interesting in relation to their color, does not appear to have been investigated. Acenaphthene-mono- and dicarboxyalkylanilides can be oxidized to naphthalene-1,8-dicarboxy-4-mono- and -4,5-dicarboxyalkylanilides,[27] which can be condensed with *o*-diamines.[28] The imides and imidazoles of 9,10-benzoyleneperylene-3,4-dicarboxylic anhydride (XII) are violet vat dyes of excellent fastness,[29] and the naphthastyril types (XIII) yield gray shades.[30]

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[20] IG, BP 447,286.

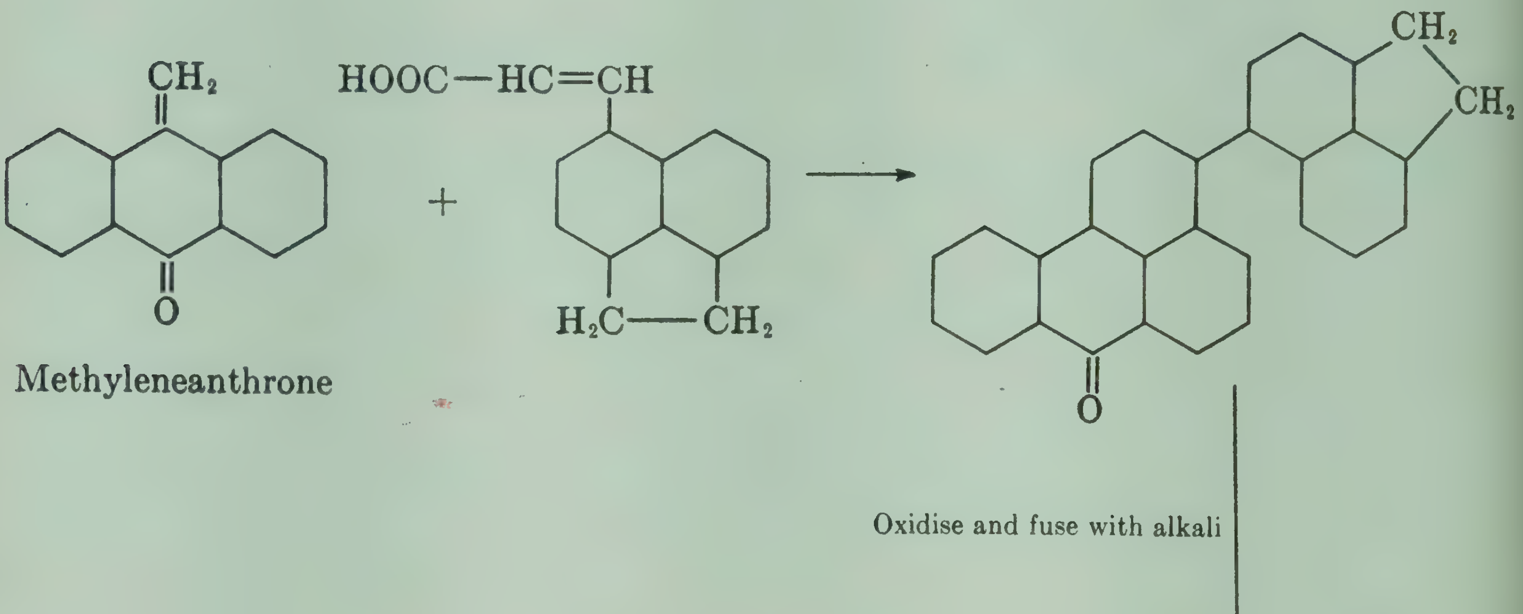
[21] IG, BP Appl. 23,231/36.

[22] IG, BP 416,385.

[23] IG, FP 852,254.

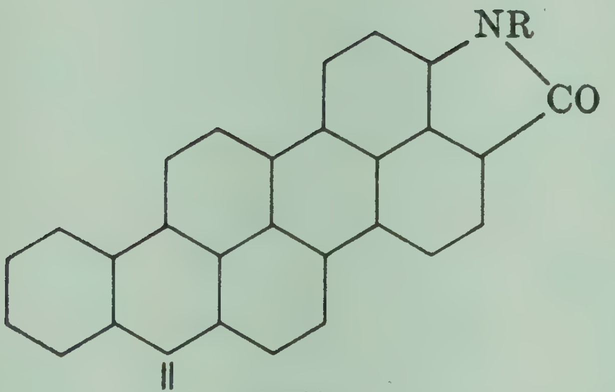
[24] IG, BP 404,867.

[25] Rodd, *Annual Repts. Soc. Chem. Ind. London* **20,** 153 (1935).

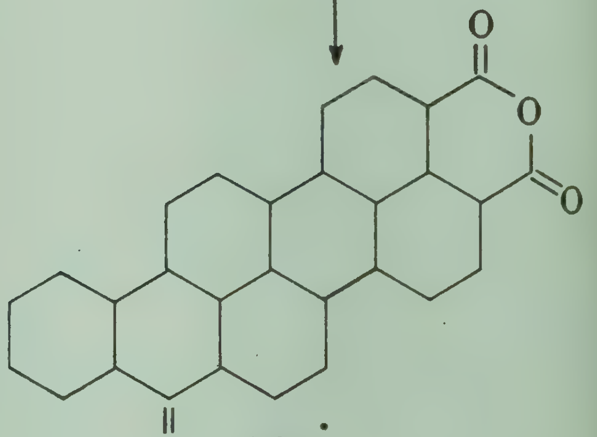


Methyleneanthrone

Oxidise and fuse with alkali



(XIII)



(XII)

The condensation of 2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic acid with excess of aniline, so as to replace the halogen atoms by anilino groups, gives a deep blue dye.[31]

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[26] IG, BP 308,651; 399,724.

[27] Wyler, Kershaw and ICI, BP 440,733.

[28] Wyler, Kershaw and ICI, BP 442,529.

[29] IG, DRP Anm. J. 51,486.

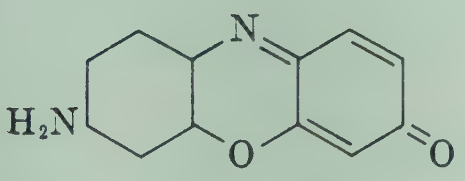
[30] IG, DRP Anm. J. 50,613.

[31] Vollmann and General Aniline Works, USP 2,087,133.

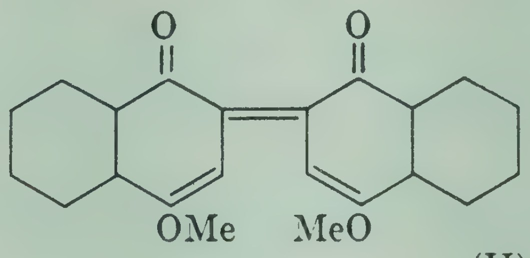
OXIDATION COLORS

Aniline Black has been considered in Chapter XXV since it is a phenazine derivative. While it is the only important oxidation color so far as textile dyeing and printing are concerned, the method of oxidizing amines, phenols, and aminophenols on the fiber is largely used for fur dyeing,[32] and the coloring matters formed are of undetermined constitution. The amines chiefly used are *p*-phenylenediamine, *o*-aminophenol and *p*-aminophenol; the first is especially important for blacks. These intermediates for fur dyeing are sold under various names such as Ursols and Paramines (IG), Durafurs (ICI), Furreins (Cb), and Fur Dyes (Calco). Precautions are necessary in handling them in view of the danger of dermatitis.

p-Phenylenediamine is widely used as a hair dye in spite of its liability to produce dermatitis of the scalp in some persons. Applied in conjunction with hydrogen peroxide or urea peroxide, the reaction on the hair is the formation of complex azines, giving dull brown, gray and black shades.[33] Brighter shades are obtained by using resorcinol or catechol together with *p*-phenylenediamine; and the reaction then appears to proceed through an indophenol, leading ultimately to an oxazone (I).[34]



(I)



(II)

1,2-Diaminonaphthalene-5-sulfonic acid, oxidized with ferric chloride and chlorine, gives an iron-containing pigment marketed as Hansa Green GS (IG).[35]

Reddish blue shades, fast to light and ironing, are obtained by padding fur with an alkaline solution of 1-hydroxy-4-methoxynaphthalene and oxidizing cold under weakly alkaline conditions for several hours. The constitution (II) has been suggested for the dyestuff formed.[36] Wool can be dyed brown with the colorless 2,4,5-trihydroxytoluene; in presence of ferrous iron an almost black iron complex is formed.[36a]

[2] Parkin, *J. Soc. Dyers Colourists Jubilee Vol.* 1934, p. 203; Beeley, *J. Soc. Dyers Colourists* **49,** 218 (1933). See also Ginzel, *Melliand Textilber.* **29,** 384 (1948).

[3] Cox, *Analyst* **59,** 3 (1934).

[4] *Analyst* **65,** 393 (1940).

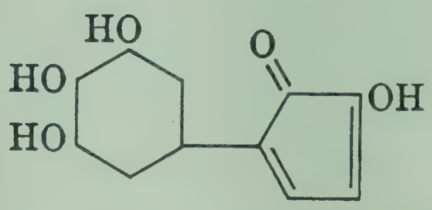
[5] *Bibliography of Scientific and Industrial Reports, U.S. Dept. of Commerce* 7 (1947).

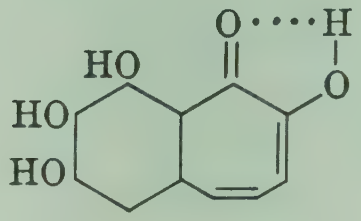
[6] IG, BP 407,066.

[6a] Burton and Stoves, *J. Soc. Dyers Colourists* **66,** 474 (1950).

Purpurogallin, produced by the oxidation of pyrogallol, crystallizes in orange-red needles (m.p. 272–273.5° on rapid heating); the substance changes in color to an intense blue on shaking with air in alkaline solution. The coloring matters of many galls contain purpurogallin glycosides.[37] Willstätter's structure (III)[38] for purpurogallin has recently been shown to be untenable by Barltrop and Nicholson,[39] who have adduced evidence in favor of (IV) which contains a seven-membered tropolone ring. Oxidation of *O*-tetramethylpurpurogallin gives 3,4,5-trimethoxyphthalic anhydride. The structure (IV) has been confirmed by synthesis.[39a]

(III)



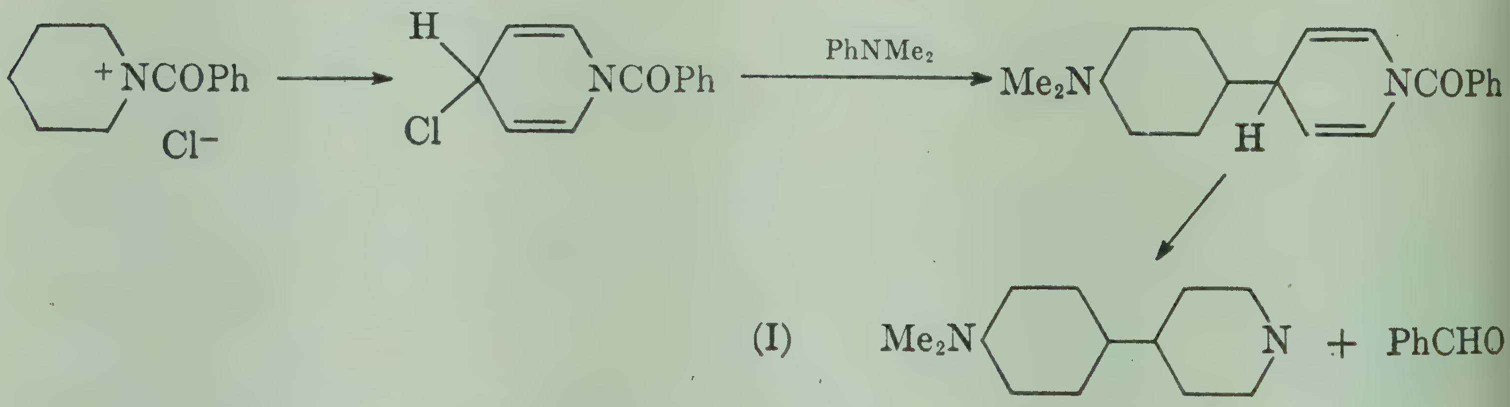


(IV)

Canarin is a yellow coloring matter of unknown constitution obtained by heating potassium thiocyanate, chlorate and hydrochloric acid; it can be produced directly on the fiber, e.g., by printing a mixture of ammonium thiocyanate and an alkali chlorate.[39b]

Pyridine and Quinoline Derivatives

p-Alkyl- and *p*-aralkyl-aminophenylpyridines have been suggested as intermediates for dyes.[40] Thus by heating dimethylaniline with a mixture of pyridine and benzoyl chloride in presence of copper bronze, dimethylaminophenylpyridine (I) is formed, probably by the indicated mechanism.[41] When (I) is converted into the pyridinium salt with benzyl



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[37] Nierenstein and Swanton, *Biochem. J.* **38,** 373 (1944).

[38] Willstätter and Heiss, *Ann.* **433,** 17 (1923).

[39] *JCS* 116 (**1948**); see also Haworth, Moore, and Pauson, *ibid.* 1045; Cook and Somerville, *Nature* **163,** 410 (1949).

[39a] Caunt *et al., JCS* 1631 (**1950**).

[39b] Torinus, *Melliand Textilber.* **31,** 847 (1950); Schmid, *Bull. soc. ind. Mulhouse* **87,** 67 (1921); sealed note 1896.

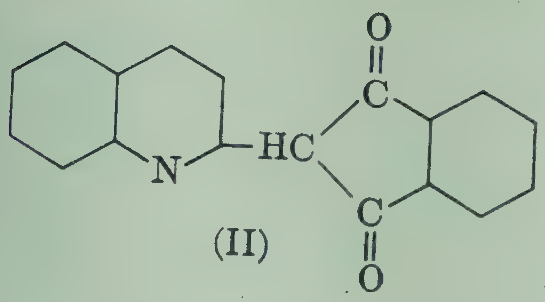
[40] IG, BP 445,781.

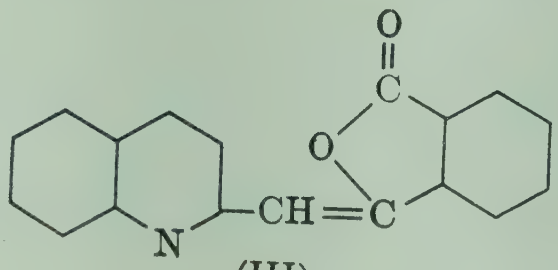
[41] Koenigs and Ruppelt, *Ann.* **509,** 142 (1934).

chloride and then sulfonated, a dye which gives greenish yellow shades on wool and silk is obtained.

Dyes derived from quinoline[42] are useful mainly as photographic sensitizers,[43] but a few are valuable for wool and silk dyeing and for coloring oils, lacquers and varnishes.[44] Quinaldine (2-methylquinoline) and its derivatives, which are intermediates for this small group of dyes, are synthesized by the Skraup reaction in which crotonaldehyde is condensed with aniline in presence of nitrobenzene, concentrated sulfuric acid and an oxidation catalyst such as vanadium pentoxide; or the Doebner-Miller reaction in which acetaldehyde and aniline are condensed in presence of hydrochloric acid or zinc chloride. By using a derivative of aniline (e.g. *p*-toluidine) the corresponding quinaldine derivative (e.g. 6-methylquinaldine) is obtained. Quinaldine has a reactive methyl group, and Quinoline Yellow (AGFA; CI 800) (Jacobsen, 1882) (golden yellow needles, m.p. 240°) is prepared by heating quinaldine with phthalic anhydride at about 220° for a few hours in presence of zinc chloride. The greenish yellow, spirit-soluble pigment is used, notwithstanding its ow tinctorial power and light fastness.

The constitution of Quinoline Yellow (Quinophthalone) was first regarded as a choice between 2-quinolylindandione (II) and the phthalide


(II)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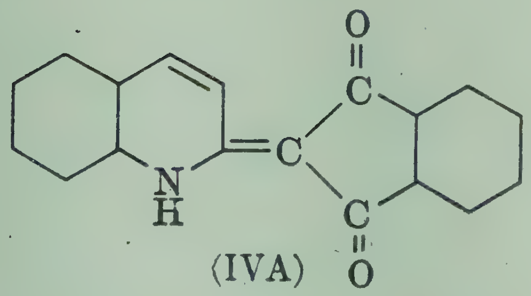
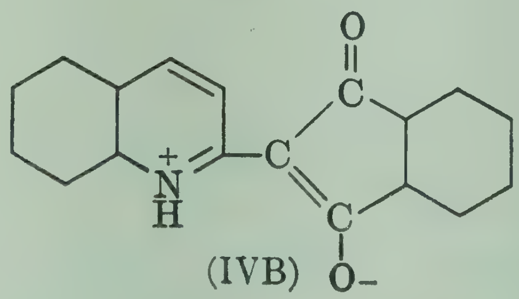

(IVA)


(IVB)

lerivative (III). Eibner's work[45] indicated that (III) is formed in the eaction, but changes to (II). The color and other properties of Quinoine Yellow, however, are better explained by regarding it as a resonance ybrid of structures such as (IVA) and (IVB).[46] Support for structure

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[2] Hewitt, Dyestuffs derived from Pyridine, Quinoline, Acridine and Xanthene, Longmans, London, 1922.

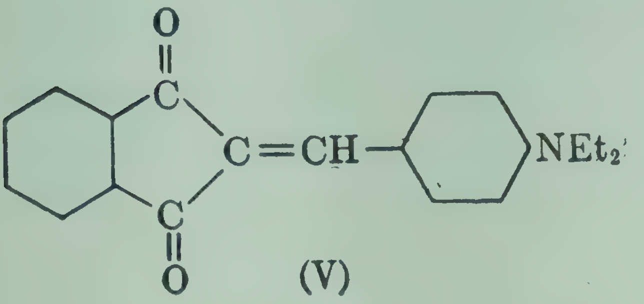
[3] See Chapter XXXVIII.

[4] For examples of azo dyes derived from quinoline, see Chapter XXI.

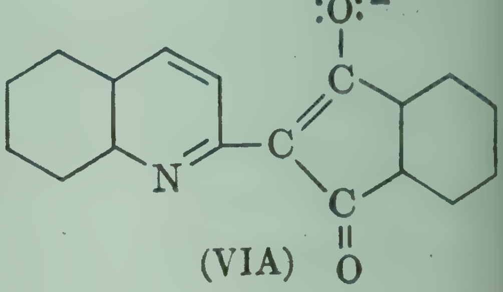
[5] Eibner and Hofmann, *Ber.* **37,** 3011 (1904); and earlier papers.

[6] Cf. Mehta, Dissertation, Univ. of Bonn., 1937.

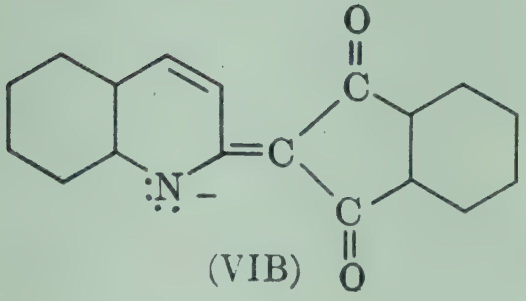
(IV) is found in the deep red color of the benzylidene-indandione (V).[47] With sodium ethoxide Quinoline Yellow forms a red sodio-derivative, and



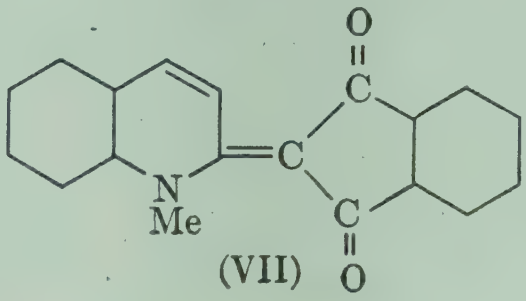
(V)



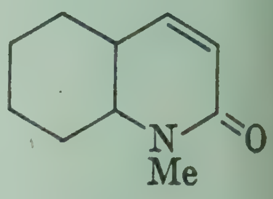
(VIA)



(VIB)



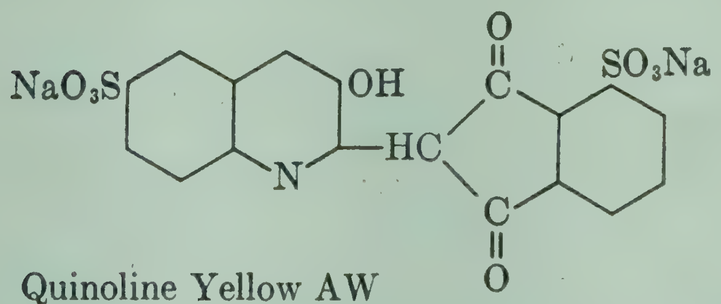
(VII)



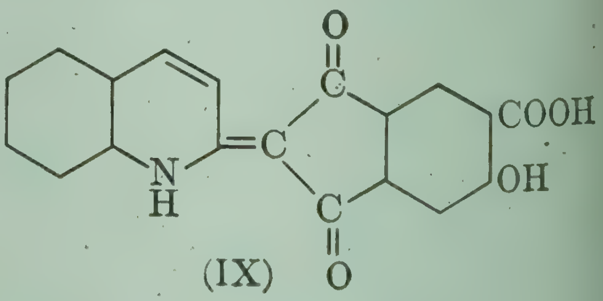
(VIII)

the deepening of color arises from the resonance of the anion among structures such as (VIA) and (VIB). The sodio-derivative is readily hydrolyzed by water. Treatment of the sodio-derivative with dimethyl sulfate in xylene at 100° gives a methyl derivative (VII), which has the properties of an *N*-methyl, rather than a *C*-methyl compound; oxidation yields *N*-methyl-2-quinolone (VIII) and phthalic acid.[48] Quinoline Yellow forms a deep red salt with concentrated sulfuric acid or hydrobromic acid, this deepening of color being associated with resonance of the cation among oxonium, carbonium, and ammonium structures.

The mono-, di- and trisulfonic acids, obtained by sulfonating Quinoline Yellow or the homolog from 6-methylquinaldine with oleum at 65–115°, are acid colors (Quinoline Yellow extra and Quinoline Yellow S extra)[49] (CI 801), which dye wool and silk in attractive, pure yellow shades with poor fastness to light. The sulfonated Quinoline Yellows are also used for the production of lakes. Quinoline Yellow KT (By) (Meyer, 1907; CI 802), prepared in a similar manner from 6-chloroquinaldine, has better fastness to light. Quinoline Yellow AW (Supra Light Yellow GGL) (IG) (ST Erg. II, p. 262) is prepared[49] by condensing 3-hydroxyquinaldine-4-carboxylic acid with phthalic anhydride, followed



Quinoline Yellow AW



(IX)

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[47] Bottke, Dissertation, Univ. of Bonn., 1931.

[48] Kuhn and Bär, *Ann.* **516,** 143 (1935).

[49] *BIOS* **961.**

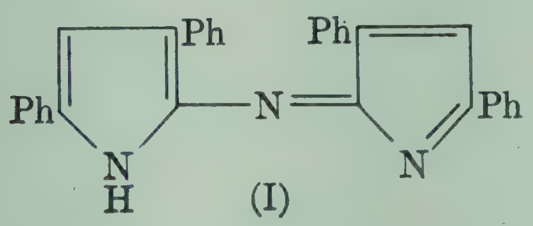
by sulfonation; decarboxylation takes place during the first reaction. Such 3-hydroxyquinaldine derivatives have better light fastness than the corresponding quinaldine dyes.[50] The naphthalene analog of Quinoline Yellow, made from β-naphthoquinaldine, gives Quinoline Yellow KT extra conc. (IG)[49] on sulfonation with 65% oleum at 35°. 6- and 8-Phenylquinaldines can be prepared by condensing crotonaldehyde with 4- and 2-aminodiphenyls; by condensation with phthalic anhydride they yield quinophthalones and yellow dyes after sulfonation.[51]

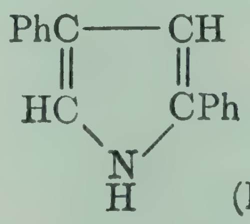
The sulfur trioxide addition compounds of quinophthalones, when heated under reduced pressure at 170–190°, give the monosulfonic acids, which have a higher tinctorial value than the mixtures of mono- and di-sulfonic acids obtained by the usual sulfonation process. The products dye wool very level yellow shades from an acid bath.[52]

Using 5- or 3-hydroxytrimellitic anhydride in place of phthalic anhydride for condensing with quinaldine, the product (e.g. IX) contains a chromable salicylic acid group, and after sulfonation gives an acid dye which can be afterchromed to a fast yellow shade. Instead of quinoline and its derivatives, such compounds as 2-methylbenzothiazole, -benzimidazole and -benzoxazole can be used.[53]

Dyes from 2,4-Diarylpyrroles

Rogers has found that the action of ammonium formate on γ-nitro-β-phenylbutyrophenone gives an intense blue pigment, which he has shown to be 2,2′,4,4′-tetraphenylazadipyrromethine (I).[54] Like the phthalocyanines, it forms metallic complexes. Hydriodic acid degrades (I) to 2,4-diphenylpyrrole (II), and the action of nitrous acid on (II) gives 5-nitroso-2,4-diphenylpyrrole which reacts with a further molecule of (II) to regenerate (I). The nitroso compound can be catalytically reduced to 5-amino-2,4-diphenylpyrrole. Derivatives of (II) can be sulfonated. The 2,4-diphenylpyrroles form methines by the usual methods of condensation with ethyl orthoformate, or by condensation


(I)


(II)

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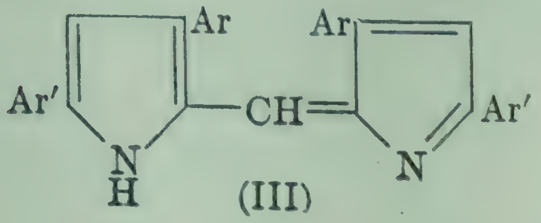
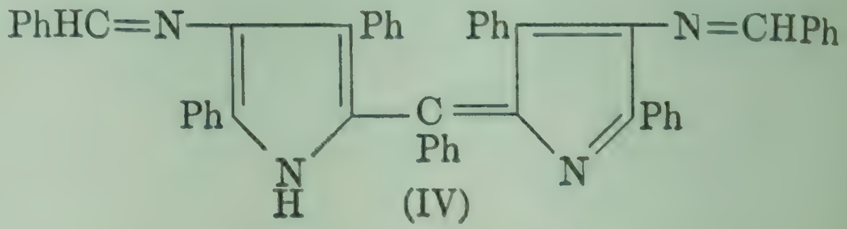
[50] IG, BP 429,176.
[51] Kyrides and Monsanto, USP 2,211,662.
[52] IG, BP 445,201.
[53] IG, BP 471,489.
[54] Rogers, *JCS* 590, 596, 598 (**1943**).

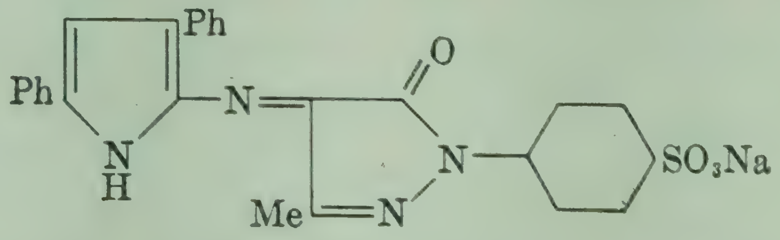
of the 5-aldehyde with a second mole of 2,4-diphenylpyrrole. The general type is (III), of which examples have been described, and these


(III)


(IV)

also form metallic complexes. The blue compound obtained by Gabriel[55] by the action of benzaldehyde and air on 3-amino-2,4-diphenylpyrrole belongs to this group, and probably has the structure (IV).

A series of dyes of the pigment, basic, and acid wool classes, derived from 2,4-diarylpyrroles, have been described in patents.[56] The basic reaction consists in treating 2,4-diarylpyrroles, which may have alkyl, aryl, or acylamido groups at 3, either with reagents such as ethyl orthoformate or benzotrichloride, capable of linking two molecules by a =CR link, or with a 2,4-diarylpyrrole having a CO group at 5; the products are tetraaryldipyrromethines. Thus 2,4-diphenylpyrroledisulfonic acid may be condensed with 5-formyl-2,4-diphenylpyrrole to give a reddish blue wool dye. Dyes of this type, or the corresponding aza compounds, form copper and other metal complexes, which can be made in substance or on the fiber. The quaternary ammonium salts of the tetraaryldipyrroazamethines may also be used as wool dyes and converted into the metal salts on the fiber. The 5-nitroso-2,4-diarylpyrroles may be condensed with compounds having a reactive methyl or methylene group, such as 1-*p*-sulfophenyl-3-methyl-5-pyrazolone, giving a bright brown-violet acid wool dye (V); 1,3,3-trimethyl-2-methylenedihydroindole gives a base,


(V)

the salts of which dye tanned cotton blue. Many examples of this type are quoted. Similarly, the 5-formyl-2,4-diarylpyrroles may be treated with reactive methyl- or methylene-containing substances such as *N*-methyloxindole, quinaldine methiodide, or 1,2,3,3-tetramethyldihydroindole; the salts of the resultant products dye in varied colors, chiefly bluish reds on tanned cotton. 2,4-Diarylpyrroles with the 5-position free, condensed with nitroso compounds such as 4-nitroso-1-aryl-5-

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[55] *Ber.* **41,** 1138 (1908).

[56] Rogers and ICI, BP 562,754–61; USP 2,410,604; Goodings, Rogers and ICI, USP 2,422,667–8; 2,434,039; 2,437,465.

pyrazolones, 3-nitrosoindoles, or *p*-nitrosodialkylaminobenzene, or with aldehydes derived from heterocyclic compounds containing nitrogen (e.g. 1,3,3-trimethyl-2-formylmethylenedihydroindole), give orange to red dyes for wool. The reactant can also be a *p*-dialkylaminodiphenyl ketone (such as 4,4′-bis-dimethylaminobenzophenone) or aromatic aldehydes (e.g. benzaldehyde, *p*-dimethylaminobenzaldehyde); the salts of the products are wool blues. Azo dyes have also been prepared.[57] Di- and tetrasubstituted 2-pyrroleazamethine dyes, which are stable blue dyes useful in color photography, can be prepared by the interaction of the appropriate propionitrile with hydroxylamine hydrochloride; thus (I) is obtained from α-phenyl-β-benzoylpropionitrile.[57a]

COLOR FORMERS IN PHOTOGRAPHY[58, 59, 60]

Colored photographs have been produced by several methods. Using for the primary development process the reduction of exposed silver halide grains to metallic silver, one method consists in incorporating in the emulsion layer a "coupler" or "color former" which condenses with the oxidation products of the developing agent to form a dye.[61] R. Fischer (1912) suggested the use of a monopack in which three color-sensitive layers are coated on top of each other: (1) bottom layer, sensitive to red, containing a cyan-producing coupler; (2) middle layer, sensitive to green, containing a magenta-producing coupler; and (3) top layer, sensitive to blue, containing a yellow-producing coupler.[61] The sensitivity of the three layers to the three regions of the spectrum is produced by incorporating suitable sensitizing dyes in the emulsion. There were various technical difficulties such as the diffusion of the sensitizing dyes from layer to layer, but these were ultimately overcome. Non-wandering sensitizing dyes were discovered, and AGFA evolved high molecular couplers which were practically incapable of diffusing through gelatin.[62]

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[57] See Chapter XI.

[57a] Knott and Eastman Kodak, USP 2,469,830.

[58] See Mees, The Theory of the Photographic Process, Macmillan, New York, 1942; especially Chapter XXIII on Spectral Sensitivity by Brooker and Carroll; Chapter XXIV on The Sensitizing and Desensitizing Dyes by Brooker; and Chapter XXV on The Mechanism of Optical Sensitizing.

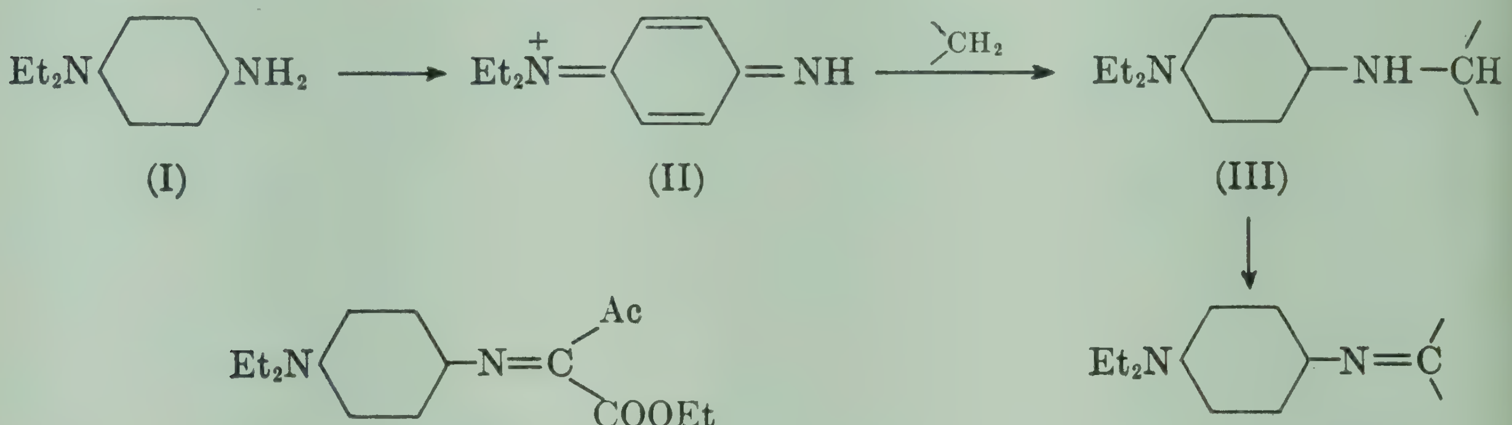
[59] James and Higgins, Fundamentals of Photographic Theory, Wiley, New York, 1948.

[60] Smith and James, *Photography* in Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. IX, Longmans, London, p. 577.

[61] Fischer and Siegrist, *Phot. Korr.* **51,** 18 (1914).

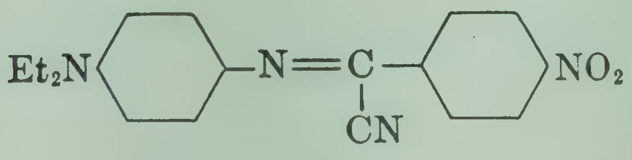
[62] For a discussion of the problem of the diffusion of color couplers, see Schneider, Fröhlich and Schulze, *Die Chemie* **57,** 113 (1944); see also Fröhlich, Schneider, Wilmanns, and General Aniline and Film, USP 2,343,051; Woodward and du Pont, USP 2,415,381–2; du Pont, BP 578,666.

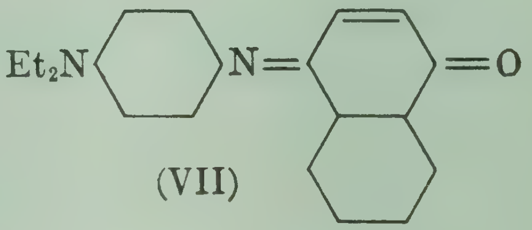
Kodacolor films utilize the same principle, but the couplers are dissolved in organic solvents and then dispersed in the emulsions. In the Kodachrome multilayer process of color photography the emulsion layers do not contain the color formers; both the color developers and couplers are present in the developing solutions. The chief developing agent is *p*-aminodiethylaniline (I) or *p*-aminodimethylaniline, and the coupler is a phenol, naphthol or a compound containing a reactive methylene group. The mechanism of the reactions which result in the formation of an indophenol (indoaniline)[63] or azamethine type of dye is by no means clear, but the intermediate stages of the quinone-diimine ion (II) and the leuco base (III) are apparently involved.[58] Semiquinone ions are probably further intermediate stages. The overall equation is (I) + $-CH_2-$ + $4Ag^+ \rightarrow$ (IV) + 4Ag + $4H^+$. Thus ethyl acetoacetate and (I) give


(I) (II) (III)

(V) (IV)

a yellow dye probably constituted as (V); *p*-nitrobenzyl cyanide the magenta-colored azamethine (VI); and α-naphthol the greenish blue


(VI)


(VII)

indophenol (VII). Esters of 1-hydroxy-2-naphthoic acid, as color formers with *p*-aminodiethylaniline, have been recently examined.[64] In view of their increasing use as cyan dye images in color photography the preparation and absorption characteristics of a series of indoaniline dyes from *p*-aminodimethylaniline and various phenols have been investigated by Vittum *et al.*[65] Phenols bearing *para*-halogen, $-COOH$, $-SO_3H$, $-OR$, $-CHOH-R$, or $-RCR'-$ groups react more or less readily to yield *p*-indoaniline dyes by elimination of the *para*-substituent. When *p*-hydroxybenzyl alcohol is used as coupler, formaldehyde is formed during development and it exerts a tanning effect on the gelatin of the emulsion. The ease with which the elimination coupling occurred appeared to be influenced by the presence of other substituents in the phenol ring. No evidence of *o*-indoaniline dye formation was observed with any of the phenols studied. In the replacement of a *p*-alkoxy group and the inability to form *o*-indoanilines, this reaction differs from diazonium coupling.[57]

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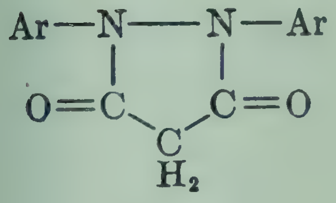
[63] Fischer, USP 1,102,028.

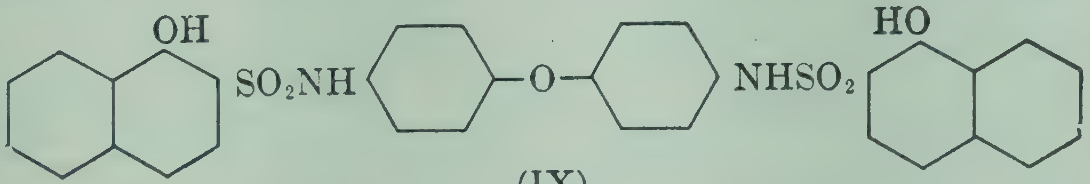
[64] Pianka and Barany, *JCS* 309 (**1948**).

[65] *JACS* **68,** 2235 (1946); **69,** 152 (1947); **71,** 2287 (1949); **72,** 4947 (1950); USP 2,476,008. See also Ziegler *et al.*, *Monatsh.* **80,** 759 (1949). The relation between color and constitution in a series of pyrazolone azamethine dyes has been studied by Brown *et al.*, *JACS* **73,** 919 (1951).

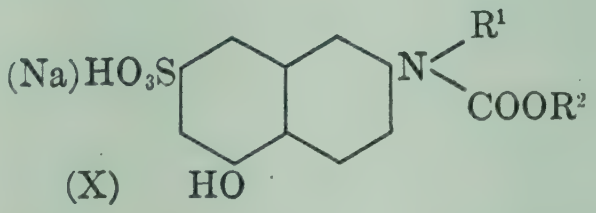
Numerous compounds have been suggested as color-forming coupling components,[66] and among these may be mentioned *N*-2-furoyl 1-amino-7-naphthol,[66a] 5-cyanacetamido-1-naphthol,[66b] 3,5-diketopyrazolidines (VIII), prepared by the condensation of hydrazobenzenes with diethyl malonate in presence of sodium ethoxide;[67] 2,5-diketopyrazolo-[2,3]pyrimidine,[67a] the condensation product of 2-methylbenzothiazole methiodide with acetoacetic ester;[67] 1-naphthol-2-sulfonyl derivatives such as (IX);[68] methylenebisthiobarbituric acid;[69] and urethanes (X) derived from J-acid in which the azamethine coupling takes place in the 6-position, R^2 being an alkyl group of at least twelve carbon atoms as a result of which (X) is nondiffusing in the emulsion.[70] The use of phenol-formaldehyde condensates[71] as resinous couplers has been proposed.[72] Phthalic anhydride reacts with acetic anhydride to form phthalidene-



(VIII)



(IX)



(X)

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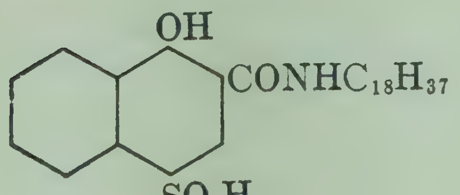
[66] For a review, see Tull, *Phot. J.* **85,** 13 (1945).
[66a] General Aniline and Film, BP 639,697.
[66b] Salminen and Weissberger, USP 2,507,180.
[67] Kendall and Fry, USP 2,427,910–1; see also 2,394,067–9; and BP 577,260; 576,890.
[67a] Bavley and General Aniline and Film, USP 2,481,466.
[68] du Pont, BP 577,387.
[69] Mueller, Bavley and General Aniline and Film, CP 449,834–5.
[70] Tulagin and General Aniline and Film, USP 2,445,252; BP 640,109. See also BP 640,122; IG, BP 465,823; 479,838; 483,000; 489,093.
[71] IG, BP 489,161.
[72] IG, BP 489,274; 535,341; 543,290; 562,675. See also du Pont, BP 635,294.

acetic acid; anilides of this acid give yellow dyes on coupling with oxidized *p*-aminodiethylaniline, and polymeric color formers, which are fast to diffusion in colloid layers of photographic elements, are produced by reaction with polymers containing hydroxyl groups.[72a] An interesting suggestion is the use of protein color formers; thus saligenin, formaldehyde and zein are condensed together and cast into a transparent film which is a blue-green color former.[73] When the polyamide prepared from bis-aminopropyl ether and adipic acid is dissolved in formic acid, treated with saligenin and precipitated by acetone, the product contains one *o*-hydroxybenzyl group per six amide groups, and forms a blue-green dye upon color coupling development of silver salts with *p*-aminodiethylaniline.[74] The replacement of gelatin by synthetic resins capable of functioning as color formers is an important development.

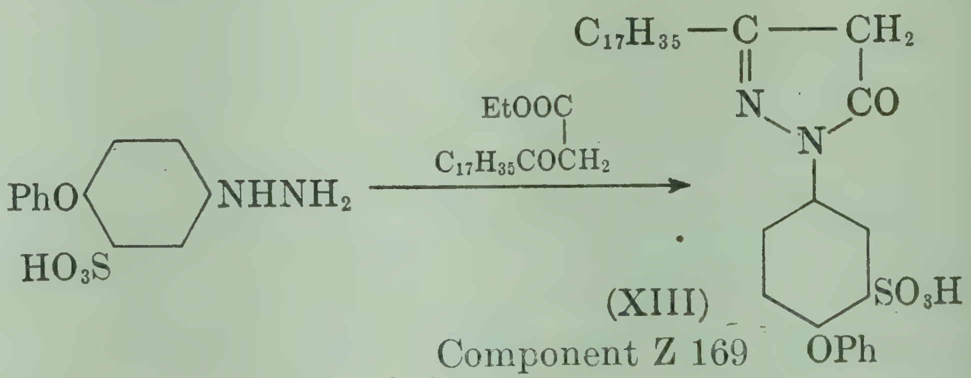
1-Aryl-2-arylsulfonylhydrazines (Ar—NH—NH—SO_2—Ar′) (XI) can be prepared by condensing an arylhydrazine with an arylsulfonyl chloride, or an aryldiazonium chloride with an arylsulfinic acid in presence of potassium carbonate and reducing the diazonium sulfinate to (XI) by means of zinc and acetic acid. When a photographic film is exposed, developed and processed in a solution containing (XI) and a Naphtol AS type of coupling component, an azoic dye image is produced. Thus when the diazonium salt for (XI) is from Fast Blue Base BB and the Naphtol used is Naphtol AS—SW, a blue azoic dye image is formed.[75]

Some of the color formers used by the IG in the preparation of the New Agfa color films have been disclosed recently.[76] The process of building up the color film was to spread the following layers successively on the film base: (1) an anti-halation layer of Helio Fast Green HG



(XII)

Component F 546



(XIII)

Component Z 169

[72a] Leekley and du Pont, USP 2,472,666.

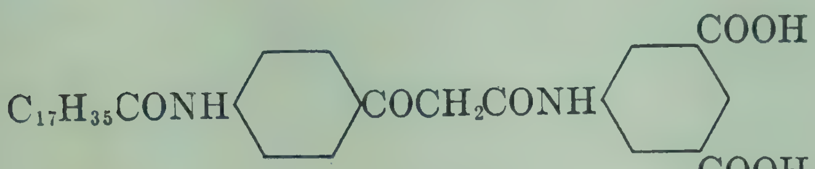
[73] Jennings and du Pont, USP 2,397,867; see also BP 484,698; Kirby and du Pont, BP 556,768.

[74] McQueen and du Pont, USP 2,428,108; see also du Pont, USP 2,396,275; 2,396,864–7; 2,463,838; 2,473,403.

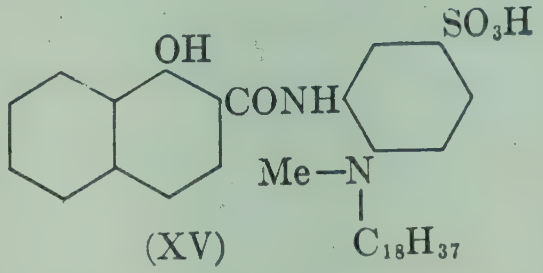
[75] Schmidt, Sprung and General Aniline and Film, USP 2,424,256. See also USP 2,495,000.

[76] *BIOS* **1157.** The theoretical and practical aspects of the Agfa color monopack subtractive process of color photography have been described in *FIAT* **976** and **977**; see also *FIAT* **721.**

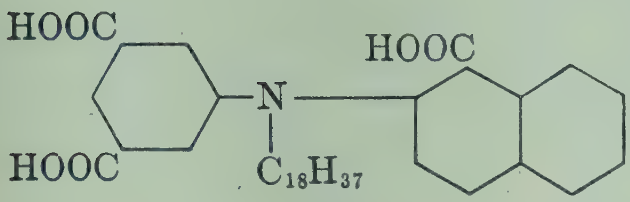
(Hansa Green GS); (2) a layer containing the bluish green component (XII) sensitive to the red rays; (3) a magenta layer of the component (XIII) sensitive to the green rays; (4) a yellow filter layer, stated to contain colloidal silver; and (5) the top layer of the component (XIV)


(XIV)

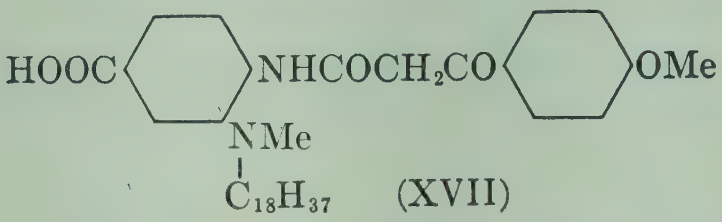
Component F 535


(XV)

Component F 654

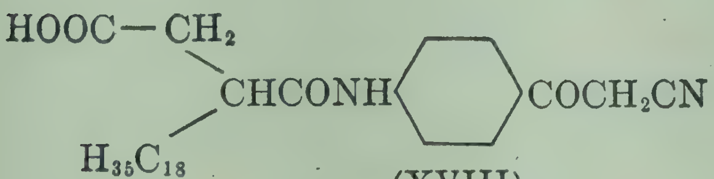

(XVI)

Component Ko 686

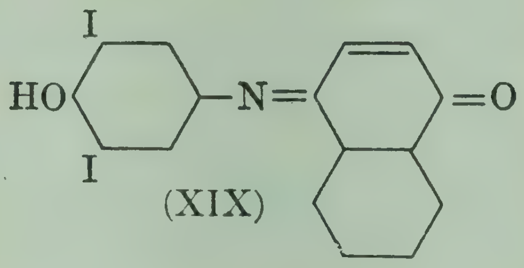

(XVII)

Component Ta 521

which is yellow and sensitive to blue rays. The content of coupler, which had to be of very high purity, was 15 g./kg. emulsion. Other cyan components which have been mentioned are (XV) and (XVI); and other yellow components (XVII) and (XVIII). There was no diffusion of the


(XVIII)

Component Koe 302


(XIX)

couplers between the layers, and the interposition of a gelatine layer between a pair of color layers was unnecessary. The blue-green and magenta layers also contained sensitizers of the cyanine type.

The coupler may be colored, e.g. a compound containing an azo-substituted reactive methylene or ethanol group;[77] the azo group is expelled during the coupling reaction. The colored couplers are such that they absorb the colors which the dyes formed from them absorb outside the range of absorption for which they are intended; thus a cyan dye would be ideal if it absorbed red light only, but it usually absorbs some green and blue light, and the colored coupler is so chosen that it absorbs the same amount of green and blue light.[78] "Automatic masking" is thus obtained in a negative-positive process.

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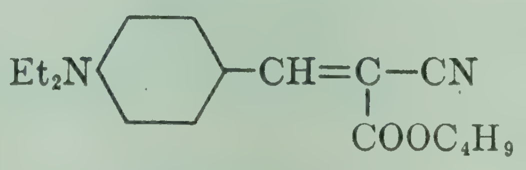
[77] Jelley, Vittum and Eastman Kodak, USP 2,434,272; see also USP 2,428,054; 2,449,966; 2,453,661; 2,455,169; Vittum *et al.*, *JACS* **72,** 1533 (1950); Merck, *Science et inds. phot.* **21,** 45 (1950).

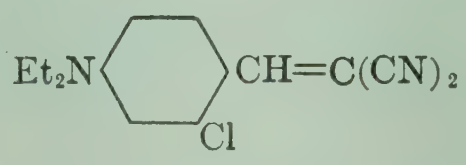
The formation of azamethine and indophenol dyes has also been utilized in making toned prints.[58] Thus a blue tone is produced by using 2,6-diiodo-4-aminophenol and α-naphthol, owing to the formation of the indophenol (XIX). The yellow azamethines obtained by oxidizing a mixture of *p*-aminodiethylaniline and a *m*-acylacetamidobenzaldehyde acetal can be applied to textile fibers as vat dyes.[78a] The bright blue to green indophenols obtained by oxidizing a mixture of *p*-aminodiethylaniline and a *m*-(o′-hydroxy)benzamidobenzaldehyde acetal or a *m*-(*o*′-hydroxy)phenylsulfonamidobenzaldehyde acetal are also applicable as vat dyes.[78b] Azamethine dyes for paper, cellulose acetate, etc., are obtained by condensing imino-, thio-, or iminothio-phthalimidine with an aromatic hydrazine or primary amine (e.g. dehydrothiotoluidine).[78c]

Styrene Derivatives

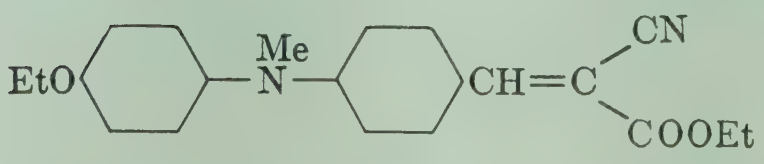
Styrene derivatives prepared by the condensation of substituted benzaldehydes with cyanoacetic esters have been suggested as cellulose acetate dyes. An example is Celliton Yellow 6G which, employed as usual in the form of an aqueous dispersion, dyes acetate rayon a greenish yellow with good light fastness (5–6).[79] Celliton Yellow 3G has excellent light fastness, but low tinctorial strength.[79] The condensation product of *p*-dimethylaminobenzaldehyde with 2-hydroxyethyl cyanoacetate dyes acetate rayon in greenish yellow shades with good fastness to light.[80] Among the IG dyes for PeCe fiber,[81] Orange D 2719 was the condensation product of 2-chloro-4-diethylaminobenzaldehyde with malononitrile.



Celliton Yellow 6G



PeCe Orange



Celliton Yellow 3G

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[78] Hanson and Vittum, *PSA Journal* **13,** 94 (1947); Hanson, *J. Optical Soc. Am.* **40,** 166 (1950).

[78a] McQueen and du Pont, USP 2,472,913.

[78b] Martin and du Pont, USP 2,472,911. See also USP 2,465,067.

[78c] Jones and ICI, BP 615,697.

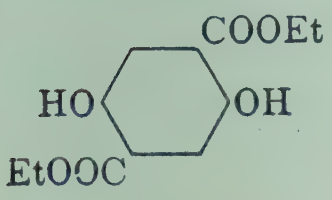
[79] *FIAT* **1313** III.

[80] Ciba, BP 586,127; USP 2,374,880; General Aniline and Film, USP 2,385,747.

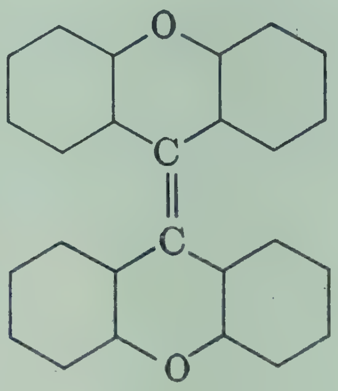
[81] *BIOS* Misc. Report **20.**

FLUORESCENT AND LUMINESCENT DYES

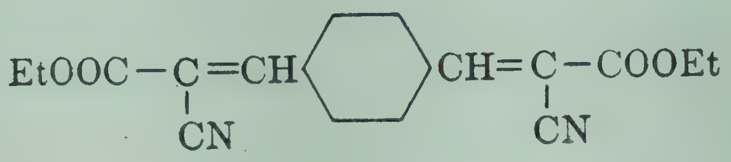
Among the dyes which luminesce on activation by ultraviolet light, used by the Germans during the war, a pyrimidanthrone derivative, Lumogen L Red-Orange, has been mentioned in Chapter XXXII. Other "Lumogen colors" (IG) belong to different chemical classes.[79, 82] Lumogen L Blue was the colorless 2,5-dihydroxyterephthalic ester (I); and Lumogen Water Blue the colorless dixanthylene (II), prepared by the action of zinc dust on xanthone. Lumogen L Yellow was 9,10-dianilinoanthracene, prepared by heating anthraquinone, aniline, aluminum chloride and zinc dust, and then acidifying with hydrochloric acid. Lumogen Yellow Orange and Brilliant Yellow were the aldazines from salicylaldehyde and 2-naphthol-1-aldehyde respectively. Lumogen Brilliant Green was (III), prepared by condensing terephthalaldehyde with ethyl cyanoacetate. Phthalylhydrazides are of interest for their chemiluminescence. An example is Luminol, prepared by treatment of 3-nitrophthalic acid with hydrazine, followed by reduction with ammonium sulfide; it has a striking bluish luminescence in dilute alkaline solution containing an oxidizing agent.[83] Aminophthalimides (e.g. 3-heptylamino-*N*-octadecylphthalimide) can be used as fluorescent dyes for artificial and natural fibers.[83a]



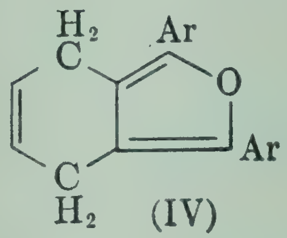
(I)



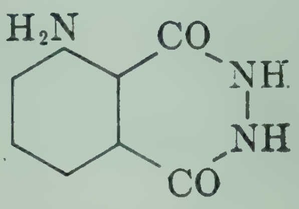
(II)



(III)



(IV)



Luminol

1,3-Diaryl-4,7-dihydroisobenzofurans (IV) are fluorescent colors for mineral oils; they are prepared by condensing butadiene and its derivatives with *s*-diaroylethylenes, and dehydrating the 4,5-diaroylcyclohexenes thus formed.[84]

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[82] *CIOS* **XXVII–84.**

[83] Curtius and Semper, *Ber.* **46,** 1170 (1913); Huntress, Stanley, and Parker, *JACS* **56,** 241 (1934).

[83a] American Cyanamid, USP 2,436,362.

[84] Adams and du Pont, USP 2,325,727.

Spinning Colors

Pigments of the azoic, Turkey Red lake, indigo, anthraquinonoid vat and phthalocyanine class were manufactured by IG in special physical form suitable for the mass pigmentation of viscose (incorporation in viscose prior to spinning). The dispersing agent mainly employed was Tamol NNO.

Lacquer Colors

Some examples of the Zapon Fast colors (IG), which are pigments for lacquers, have been mentioned in earlier chapters. The Zapons listed in Table I are salts of water-soluble azo and anthraquinone dyes with (a) cyclohexylamine, (b) dicyclohexylamine, or (c) di-*o*-tolylguanidine.

Zapon Fast Grey HL is a mixture (4:1) of Zapon Fast Blue HL (See Chapter XXXVII) and Zapon Fast Yellow CGG. The Zapons listed

TABLE I
Zapon Fast Colors

	Zapon Fast	*Constitution*
(a)	Yellow CGG	Fast Light Yellow G
	Red C2B	Anthosine 3B
	Blue CGG	*o*-Nitroaniline $\xrightarrow{\text{acid}}$ H-Acid $\xleftarrow{\text{alk.}}$ *m*-Toluidine
	Blue CR	4-Piperidino-1-hydroxyanthraquinone-2-sulfonic acid
	Violet CB	Anthraquinone Violet (Sulfonated 1,5-dianilinoanthraquinone)
	Violet CRR	Brilliant Benzo Fast Violet BL
(b)	Yellow 8431	2-Nitroaniline-4-sulfonic acid
	Scarlet CG	Brilliant Crocein
	Scarlet CR	Ponceau 5R (Aminoazobenzene → 2-Naphthol-3,6,8-trisulfonic acid)
	Scarlet CRR	Heliopurpurin 7BL (Aminoazobenzene-disulfonic acid → 2-Naphthol-3,6,8-trisulfonic acid)
	Red CB	Azo Cerise MIA (Aminoazotoluene → Acid GR)
	Brown	Sirius Supra Brown 3R
(c)	Scarlet PAJ	Brilliant Crocein B

TABLE II
Zapon Fast Colors

Zapon Fast	*Composition*
Red 3B	Rhodamine B extra + Palatine Fast Orange RN
Fire Red B	Rhodamine 4GD extra + Palatine Fast Yellow GRN
Red P1691	Rhodamine B extra + Palatine Fast Orange RN
Violet RR	Rhodamine B extra + 2 moles Palatine Fast Violet 3RN

in Table II are pigments prepared by coprecipitation of the pairs of acid and basic dyes mentioned in the second column.[85]

Pigmented Leather Finishes

The Corial and Eukanol colors (IG) are leather dyes, and a few are also applicable to paper.[79] The Corial colors are pigmented nitrocellulose base emulsions. Thus Corial Orange L consists of Permanent Red G dispersed in a lacquer made up from nitrocellulose, camphor, dibutyl phthalate, butanol, methyl and butyl acetate, methanol, xylene and polyvinyl ethyl ether. The Eukanols are dispersions of pigments (e.g., Indanthrene Blue GGSL, Permanent Yellow NCG, Lithol Fast Scarlet TRN) in sodium caseinate, with the addition of *o*-hydroxydiphenyl, Nekal A and sodium sulfanilate. Prior to the application of the Corial and Eukanol colors, which are also finishes, rough leather is dyed with water-soluble acid colors.

[85] See also Geigy, SP 230,696; 234,937–43; 236,939–40.

CHAPTER XL

THE ACTION OF LIGHT ON DYES AND DYED FIBERS

Among the properties desired in a dye, fastness to light is of great importance, and the standardization of technique for the assessment of fastness to light has received increasing attention.[1] As a result of the discovery of new types of synthetic dyes, such as the anthraquinonoid vat colors, phthalocyanines, and copper complexes of direct cotton dyes, and the accumulation of data on structural variations in a given type of dye which improve the light fastness, many dyes with very high stability to light are now available. However, there is little knowledge of the mechanism of the changes which take place when dyed materials are exposed to light, the products of photochemical degradation, and the photosensitivity of dyes in relation to molecular structure.[2, 3, 4, 4a]

Factors affecting the fastness of dyed fibers. The fastness of a dye to light or other agencies does not refer to the stability of the pure dye in the solid state or in solution, but to the fastness of a dyed or colored material such as a textile fabric. The substrate or medium to which the dye has been applied has therefore to be specified when a fastness grade is assigned to a dye. A further complication in the quantitative assessment of fading is that the change involves all the three characteristics of color—purity (or chroma), brightness (or value in the Munsell system), and less frequently, the hue (or dominant wave length).[5] The action of light on a dyed fiber depends on the nature of the dye and of the fiber, the other constituents of the dyed fiber, the composition of the atmosphere, and the source of light.[6] Cellulose, wool and other fibers are themselves acted upon by light. The changes in the dye and the fiber may be independent of each other; the character of the fiber and the fiber-dye combination may influence fading; the dye may accelerate the photochemical decomposition of the fiber; or the dye may act as a protective agent. During exposure to light under normal conditions, the dyed fiber is also subject to the action of moisture, oxygen and other constituents of the atmosphere (e.g. nitrogen oxides, sulfur dioxide, hydrogen sulfide).

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[1] See Chapter VI for an account of fastness tests and standards.

[2–4a] For reviews of the photochemistry of dyes, see (2) Ellis, Wells, and Heyroth, The Chemical Action of Ultraviolet Rays, Reinhold, New York, 1941; (3) Rodd and Abbott, Photosensitivity of Dyestuffs *in* Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. IX, Longmans, London, 1949; (4) Terenin, Photochemistry of Dyes and Related Organic Compounds, Akademiya Nauk S.S.S.R., Moscow and Leningrad, 1947; (4a) Symposium on Photochemistry in relation to textiles, *J. Soc. Dyers Colourists* **65,** 585 (1949).

[5] Seibert, *Am. Dyestuff Reptr.* **34,** 272 (1945).

[6] For a summary of the literature up to 1924 on the action of light on dyes applied to cotton fabrics, see Cunliffe, *J. Textile Inst.* **15,** T173 (1924); for a study of various factors in fading, see Cunliffe, *J. Soc. Dyers Colourists* **46,** 108, 297 (1930); **47,** 73, 225 (1931); **48,** 59 (1932). See also Vickerstaff and Tough, Lead, Burgess, Nordhammer, and Gralén in Ref. 4a.

For testing purposes a carbon arc lamp (e.g. the Fadeometer)[1] may be used, but the fading of dyed materials by light action results from exposure to direct or diffuse sunlight, which varies in intensity according to the latitude and elevation of the place at which the exposure is made, the season of the year and the time of day. In general, fading can be related to the actinic value of the light as registered on photographic sensitized film or paper.[7] Some dyes are fast to sunlight, but fade on exposure to the ultraviolet light of a quartz mercury lamp; such dyes absorb strongly in the region 2000–3200A, while dyes which are fast to both kinds of light are transparent throughout the ultraviolet (2400–3600A.).[8] Fading by the action of daylight is mainly due to radiant energy in the visible spectrum.[8a] High temperatures accelerate fading and fiber degradation. For accelerated ageing tests for light action, exposure in a Fadeometer at 63° ± 3° and relative humidity of 45 ± 15% has been recommended. Fifty hours exposure in a Fadeometer under these conditions is equal to 300 hours normal Fadeometer exposure or six months daylight exposure behind glass.[9]

High humidity usually accelerates fading, but the quantitative effect varies widely and depends both on the fiber and the dye.[6] The rate of fading of certain azo and acid triphenylmethane dyes on wool, and of basic dyes (Magenta, Brilliant Green and Safranine) on tannin-mordanted cotton, increases linearly with the moisture content of the fiber.[10]

It is well known that the fastness of a dye may be very different according as the dyed fiber is cotton, wool, silk or nylon. Wool is less sensitive than other fibers to humidity and to atmospheric action in general, and is therefore employed for dyeing standard patterns, by comparison with which the light fastness of a dyeing is graded on the 1–8 scale.[1, 6] Many vat dyes with excellent fastness on cotton fade badly on nylon, and acetate rayon dyes also exhibit inferior light fastness on nylon.[11] Several indigoid and thioindigoid dyes have better light fastness on wool than they have on cotton. Some basic dyes on cellulose acetate have better light fastness than they have on tannin-mordanted cotton. Direct cotton dyes as a class have been stated to have better light fastness on viscose.[12] The acidity or alkalinity of the fiber after dyeing and finishing may influence the light fastness.[13] The fastness of a dye varies with the strength of the shade; the heavier shades are usually faster.[14] It is therefore becoming customary to state the fastness of a dye on a given fiber in three strengths of shade (e.g. 0.25, 1 and 2.5%). If a dyeing is made with a mixture of dyes, one dye may influence the action of light on another. The fastness of a mordant dye depends on the mordant and mordanting method, because different metal-dye complexes are formed, which may differ in their stability to light, and also because the metal may have a positive or negative catalytic effect on the photochemical degradation of the dye.[15] Titanium oxide used for delustering viscose can accelerate the fading of dyes.[16]

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[7] Barker and Hirst, *J. Soc. Dyers Colourists* **43,** 324 (1927).

[8] Sisley, Rivat, and Bardet, *Rev. gén. mat. color.* **23,** 85 (1919).

[8a] Taylor and Pracejus, *Illum. Eng.* **45,** 149 (1950).

[9] Lyle *et al., Am. Dyestuff Reptr.* **37,** 251, 282 (1948).

[10] Hedges, *J. Soc. Dyers Colourists* **44,** 52, 341 (1928).

Mechanism of Fading

The absorption of one quantum of light of λ4000A (the blue end of the visible spectrum) represents an increase in the energy of the molecule of about 71 kcal; and when this is compared with bond energies (e.g. C—C 58.6; C—N 48.6; C—O 70.0; C=C 100; C=O 142–152; N=N 80 kcal per mole),[17] it is clear that light energy (especially the energy of ultraviolet radiation) is adequate for the rupture of bonds in organic molecules, assuming that all the absorbed light energy is available for this purpose. The problem therefore is not why dyes fade, but why many dyes have such remarkable stability to light.

By the absorption of light a molecule rises from its ground state of lowest energy to an excited state of higher energy in which one of the electrons is at a higher level. The life of an excited molecule, which can be estimated by various methods, is exceedingly small: about 10^{-7} to 10^{-8} sec. for a permitted transition. The activated molecule expends the energy of excitation in one of several ways.[18] It may emit radiation in the form of fluorescence or phosphorescence; or lose its energy as heat by collision with other molecules (collision of the second kind); or dissociate or take part in chemical reaction. The primary photochemical change may be followed by secondary thermal reactions, which again may take place as successive or chain reactions or branch out into several side reactions, so that the process as a whole becomes extremely complex, and interpretation correspondingly difficult.

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[11] Abbot, *J. Soc. Dyers Colourists* **60,** 55 (1944).

[12] Whittaker, *J. Soc. Dyers Colourists* **51,** 313 (1935).

[13] Seibert and Sylvester, *Am. Dyestuff Reptr.* **33,** 311 (1944).

[14] Cf. Sommer, *Z. angew. Chem.* **44,** 61 (1931); Pinte, *Chimie & industrie* **34,** 923 (1935).

[15] Bancroft and Ackerman, *Proc. Natl. Acad. Sci. U.S.* **18,** 147 (1930).

[16] Sandoz, *J. Soc. Dyers Colourists* **50,** 13 (1934).

[17] Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca, New York, 1940. See also Skinner, *Trans. Faraday Soc.* **41,** 645 (1945); Syrkin, *J. Phys. Chem. U.S.S.R.* **17,** 347 (1943).

The first law of photochemistry (Grotthuss, 1817) states that it is only absorbed light which is photochemically active. Photochemical activity with visible light is therefore associated with colored substances. While photochemical reactions can be induced only by the absorption of light, all the absorbed energy is not necessarily effective in the chemical process. According to the Einstein law of photochemical equivalence each molecule taking part in a photochemical reaction absorbs one quantum of radiant energy. The quantum yield or efficiency ϕ (number of molecules changed/number of quanta absorbed) should be unity if the Einstein law is obeyed; it varies, however, from a minute fraction (as for dyes) to millions (as for some chain reactions). The law applies only to the primary light-absorbing process; the low quantum yields arise from such causes as deactivation of the excited molecules by collision or recombination of photodissociation products. With the large, polyatomic dye molecules, internal or intramolecular deactivation mainly accounts for the low quantum efficiency of the fading process.

Considering the many different chemical types to which the synthetic dyes belong, it is clear that no single or simple mechanism can explain the fading of dyes as a class. Even with simple organic molecules, photochemical reactions of varied character are encountered, and the fading of dyes might involve three photochemical reactions—oxidation, reduction and decomposition (photolysis). In addition, photosensitization has to be considered (see later).

The fading of dyes by the action of light and air is usually an oxidation process. For many dyes the rate of fading is highest in oxygen, lower in nitric oxide and carbon dioxide, and practically zero in nitrogen or hydrogen, although changes due to reduction sometimes occur in hydrogen.[19] In oxygen and the oxide gases, carbon dioxide can be detected after exposure to sunlight, and the amount of carbon dioxide produced is much more with cotton as the substrate than with porous clay. Examining some azo dyes on wool and substantive and basic dyes on cotton, Bolis observed that fading was much more rapid in air than in evacuated glass tubes.[20] On the other hand, aqueous solutions of acid and basic triphenylmethane dyes fade as badly in nitrogen as in air.[21] The possibility of cellulose under the influence of light reacting with a dye is indicated by the observation[22] that irradiation of cellulose by ultraviolet light in a nitrogen atmosphere causes considerable degradation; the cellulose is left in "an unstable state" which facilitates further degradation on exposure to air.

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[18] For general accounts of Photochemistry, see Plotnikow, Allgemeine Photochemie, 2nd ed., Gruyter and Co., Berlin and Leipzig, 1936; Rollefson and Burton, Photochemistry, Prentice-Hall, New York, 1939; Bowen, The Chemical Aspects of Light, Oxford Univ. Press, London, 1942; and Photochemistry *in* Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. IX, Longmans, London, 1949; Noyes, Jr. and Boekelheide, Photochemical Reactions *in* Technique of Organic Chemistry, Vol. II, Interscience, New York, 1948. For a recent review of light absorption and photochemistry, including photopolymerization and the effects of light on dyes, see Bowen, *Quart. Revs.* **4**, 217 (1950). See also Livingston, Irreversible and Reversible Photobleaching of Dyes, in Ref. 4a.

The formation of peroxides on exposure to light has been noticed with several types of dyes (azoic, basic, sulfur, anthraquinonoid); but there is no definite relationship between fading and the tendency to form peroxides.[23] Gebhard[24] regarded perhydroxyl ions (HO_2^-), formed by a primary reaction between oxygen and water, as responsible for the fading of dyes. In dry air he assumed the formation of dyestuff peroxides of relatively high stability by a combination of dissociated oxygen with the dye molecules. When moisture was present, highly reactive peroxide hydrates of the type HO—Ar—OOH were formed, which reacted with unchanged molecules of the dye or with the fiber, or decomposed with the production of acids or phenols. The peroxide hydrates of dyes which are fast to light may pass into the more stable peroxide by elimination of water.

Gillet and Giot[25] have examined the oxidation mechanism of fading by observing the effect of antioxidants, such as catechol, hydroquinone, gallic acid, tannins and thiourea, on azo dyes, acid and basic triphenylmethane dyes and Rhodamines, dyed on wool and cotton. Protection of some dyes was observed, but only if large amounts of antioxidants were used, and no general conclusions could be drawn. Thiourea and a mixture of glucose and sodium metaphosphate were found by Haller and

[19] Scharwin and Pakschwer, *Z. angew. Chem.* **40,** 1008 (1927).

[20] *Rev. gén. mat. color.* **12,** 289 (1908).

[21] Ackerman, *J. Physical Chem.* **36,** 780 (1932).

[22] Stillings and Van Nostrand, *JACS* **66,** 753 (1944). See also Egerton in Ref. 4a.

[23] Haller and Ziersch, *Z. angew. Chem.* **43,** 209 (1930); *Melliand Textilber.* **10,** 951 (1929).

[24] *J. Soc. Dyers Colourists* **34,** 74 (1918); and earlier papers.

[25] *Compt. rend.* **176,** 1402, 1558, 1894 (1923); *Rev. gén. mat. color.* **27,** 98 (1923).

Ziersch to protect a number of dyes of different types on cotton.[23] Thiourea and its derivatives, dimethylolurea and other amides have been the subject of patents, especially for protecting dyed acetate rayon from light and gas fading;[26] however, except for coppering of certain direct cotton dyes, no treatment has proved to be of practical value for a substantial increase in the light fastness of fugitive dyes. On the other hand, the danger of accelerated fading owing to the presence of various substances (e.g., urea-formaldehyde resins and cation-active compounds used for improving the wash-fastness of direct dyes) in dyed fibers is of practical importance. Haller and Ziersch noticed that fading is accelerated not merely by oxidizing agents (e.g., nitrite and dichromate), but also by a variety of organic substances such as glycerol, Turkey Red oil, starch and gums. Chlorazol Sky Blue FF (Diamine Sky Blue FF) fades much more rapidly when absorbed on titanium dioxide; the quantum efficiency of the photochemical process rises rapidly as the threshold of absorption of titanium dioxide is reached.[27]

FLUORESCENCE

No direct relation between fluorescence and fading of dyes has been established, but they are related phenomena. Many dyes which have poor fastness to light are fluorescent in solution or on the fiber. Fluorescence, fading and dye-sensitized photochemical reactions are processes by which absorbed light energy is dissipated.

When energy absorbed by a substance is emitted wholly or partly as light, the phenomenon of luminescence is observed.[28, 29] The glow of phosphorus in the dark is due to chemical action (combination with oxygen) and is an example of chemiluminescence. Luminescence in the form of fluorescence occurs when absorbed light energy is reemitted as light, usually of longer wave length, while the source of excitation is still on. Thus a yellow solution of the disodium salt of Fluorescein exhibits in blue light a brilliant green fluorescence. Since the excited molecules do not usually return to the lowest vibrational level of the ground state, but to higher vibrational levels, the energy of emission is smaller than the energy of excitation, and the wave length of the fluorescence radiation is therefore greater than the wave length of the absorbed or exciting radiation. Just as the vibrational structure of an absorption spectrum corresponds to the vibrational levels of the excited state, the vibrational structure of a fluorescence spectrum indicates the vibrational levels of the ground state. There is an approximate mirror image relation between the fluorescence spectra of many compounds (e.g. polycyclic aromatic hydrocarbons) and the bands of longest wave length of their ultraviolet absorption spectra.[30]

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[26] See Chapter XXVII.

[27] Goodeve and Kitchener, *Trans. Faraday Soc.* **34**, 570, 902 (1938).

[28] Pringsheim and Vogel, Luminescence of Liquids and Solids, Interscience, New York, 1946; Pringsheim, Fluorescence and Phosphorescence, Interscience, New York, 1949.

[29] Bowen, Fluorescence and Fluorescence-Quenching, *Quart. Revs.* **1**, 1 (1947).

In phosphorescence, light emission persists, sometimes for several hours, after the excitation process has come to an end; some of the excited molecules do not return to the level corresponding to the fluorescence radiation, but pass into a state of intermediate energy which is metastable and has considerably longer life than the normal excited state.

The intensity of fluorescence of a substance in solution increases with the concentration up to a certain maximum, and then falls off at higher concentration because of an increase in the frequency of collision between excited and unexcited molecules and consequent deactivation; fluorescence quenching at high concentrations also results from dimerization or polymerization. The three processes of fluorescence, deactivation as thermal energy and photochemical reaction can take place simultaneously. Thus Eosine in solution fluoresces strongly on irradiation, and is at the same time oxidized to a colorless substance by photochemical action; the quantum efficiency of the photochemical change is low, and a large part of the energy of excitation is lost as thermal deactivation. The reason why fluorescent dyes are usually more photosensitive and fade more rapidly than nonfluorescent dyes is that the active life period of the molecules of the former is longer and the chances of collision with the oxygen of the air therefore greater.

Many dyes, which are fluorescent in aqueous solution, exhibit phosphorescence in rigid or glass-like solvents such as glycerol at very low temperature; while the average life of an excited electronic state is usually about 10^{-8} sec. the emission of light in the metastable state persists for several seconds after the exciting radiation has been cut off. Lewis has identified this long-lived upper electronic state of complex molecules with a triplet or diradical state, in which two electrons have uncoupled spins, so that transition to the normal singlet state is "forbidden."[31, 32] Kasha has established by the direct measurement of paramagnetism that the phosphorescent state of acid fluorescein is a triplet state. He has drawn attention to the great photochemical importance of the identification of metastable electronic states as triplet states; the absence of prolonged luminescence in fluid media does not always mean that there is no excitation to the metastable state, and this state may be merely deactivated.[32] The metastability of excited molecules can also arise from other causes. Terenin has suggested that the metastable biradical state plays an important part in photochemical reactions. A trace of oxygen quenches the delayed fluorescence because of reaction with the biradical. An active form of oxygen is thus produced. The labile oxide may be transformed into a peroxide, with or without the intervention of water, and the dye may then undergo oxidative degradation.

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[30] Berenblum and Schoental, *JCS* 1017 (**1946**); Schoental and Scott, *JCS* 1683 (**1949**); See also Lewschin, *Z. Physik.* **72,** 368 (1931).

[31] Lewis *et al.*, *JACS* **63,** 3005 (1941); *et seq.*

[32] See also Kasha, *Chem. Revs.* **41,** 40 (1947); Terenin, *Acta Physicochem. U.R.S.S.* **18,** 210 (1943).

While there is considerable knowledge of color-constitution relationships, the fluorescence of organic compounds has been correlated with their chemical constitution only to a very limited extent. Light absorption is necessary for photoluminescence, and the wave lengths of absorption and emission are related (Stokes law); but the light absorption characteristics of a molecule do not indicate its fluorescence properties. Aromatic hydrocarbons in general are fluorescent. Numerous heterocyclic compounds, such as coumarin, xanthene, carbazole, acridine, and their derivatives, exhibit fluorescence in solution. The introduction of halogen or nitro groups diminishes fluorescence, and an amino group increases it. A molecule may fluoresce in the neutral condition or only as a cation or an anion, and fluorescence indicators can therefore be used in volumetric analysis. Fluorescence is also greatly influenced by external conditions. Solid rubrene is nearly nonfluorescent, but in hexane solution it has a brilliant fluorescence with a quantum yield of about 100%.[33] Many dyes (e.g., of the diphenylmethane, triphenylmethane and azo series), which exhibit little or no fluorescence in solution in water, alcohol, and other liquid solvents, are strongly fluorescent when dyed on cotton, wool or silk. The fluorescence of the same dye may differ in color on different fibers; the fluorescence of Thioflavine is blue on cellulose acetate, yellow on viscose and green on silk.[29]

The use of colorless blue-fluorescing substances (e.g., Blankophors, IG) in place of blue pigments and dyes, such as Ultramarine and Alizarin Sky Blue, for "bluing" bleached cotton and linen fabrics has been mentioned in Chapter XX.

PHOTOTROPY

Marckwald (1899) defined phototropy[34] as a change in color occurring in a solid on exposure to light, the change being slowly reversed in the dark. Phototropy has since been observed in a variety of organic compounds (e.g. azo dyes, anils, semicarbazones, thiosemicarbazones),[34a] but the reasons for the occurrence of the phenomenon have not been satisfactorily explained. It would appear that a single mechanism is inapplicable to all the instances of phototropy.

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[33] Bowen and Coates, *JCS*, 105 (**1947**).

[34] For a review of phototropism in solution and on dyed textiles, see Stearns, *J. Optical Soc. Am.* **32,** 282 (1942). See also Ref. 2.

The phototropy of certain yellow and orange azo dyes on cellulose acetate and the view of Mechel and Stauffer that phototropy is due to *trans-cis* isomerism have been mentioned in Chapter XXI. In agreement with Mechel and Stauffer, Knight[34b] has observed that aminoazobenzene derivatives prepared by coupling diazotized *o*- or *p*-nitroaniline with aniline or an *N*-alkylaniline are nonphototropic, and he has suggested that this property may be associated with the stabilization of quinonoid resonance structures; analogous dyes from *m*-nitroaniline were found to be phototropic. When the stable *trans* form of azobenzene is exposed to light, the major part is converted into the *cis* form, which has been isolated and characterized (see Chapter XI). This has not been possible with amino- and hydroxyazo compounds because of the tendency of the *cis* to revert to the *trans* form. However, the stereochemistry of azo dyes has not been extensively investigated, and the evidence relating the phototropy of azo dyes on acetate rayon with *trans-cis* isomerism is not conclusive.

Examples are cited to illustrate the differences in the nature of the phenomena which have been described under the common name of phototropy.[35] Examining twenty-eight anils of 5-bromosalicylaldehyde, Brewster and Millam found that twenty-two were thermotropic and only three were phototropic.[35a] Senier and Shepherd observed phototropic change in a large number of anils, hydrazones and fulgides and ascribed it to change in aggregation.[35b] Chalkone semicarbazones exhibit "photochemical isomerism"; and chalkones undergo polymerization by irradiation; the changes are complex and only partly reversible.[35c]

[34a] Examples of phototropic inorganic compounds are dithiotrimercuric salts (2HgS, HgX_2), which are dissociated by light, forming black HgS and HgX_2; in the dark the system loses radiant energy and the original compound is reformed; Rao *et al.*, Nature **124,** 303 (1929); *J. Phys. Chem.* **32,** 1354 (1928).

[34b] *J. Soc. Dyers Colourists* **66,** 175 (1950).

[35] For miscellaneous examples of phototropy see (*a*) *JACS* **55,** 763 (1933); (*b*) *JCS* **95,** 441, 1943 (1909); (*c*) Stobbe *et al., J. prakt. Chem.* **123,** 1 (1929) and other papers; (*d*) Heilbron, Hudson, and Huish, *JCS* **123,** 2273 (1923); (*e*) *Bull. soc. chim.* **1,** 97 (1934); **53,** 1441 (1933); *Rev. Stiint. "V. Adamachi"* **32,** 255 (1946); (*f*) *Ann. sci. univ. Jassy* I, **29,** 17 (1943); (*g*) Reimer, *JACS* **58,** 1108 (1936), and earlier papers; (*h*) *Trans. Faraday Soc.* **27,** 478 (1931); *JACS* **43,** 333 (1921); (*i*) Lifschitz, *Ber.* **52,** 1919 (1919); (*j*) Singh and Dutt, *J. Indian Chem. Soc.* **19,** 130 (1942); (*k*) *J. Indian Chem. Soc.* **15,** 573 (1938); (*l*) Child and Smiles, *JCS* 2696 **(1926).**

Cinnamaldehyde semicarbazone exhibits "reversed phototropy"; after exposure to diffuse sunlight for some hours, if the substance is placed in the dark a yellow color develops, which again disappears on re-exposure to light.[35d] Gheorghiu[35e] found that semicarbazones of ketones of the type ArCH=CHCOR obtained by the alkali condensation of methyl ketones with aromatic aldehydes are phototropic, but not those of the ketones ArCH=CRCOCH$_3$ obtained by acid condensation. He has suggested that phototropy is due to a displacement of π-electrons and changes disturbing the conjugation in a molecule tend to diminish or eliminate the phenomenon; substituents in the benzene ring capable of resonance favor phototropy; the state of the colored molecule is an intermediate state resulting from the superposition of several limiting structures. According to Matei ketones which form nonphototropic semicarbazones do not form phenylhydrazones, but pyrazoline derivatives, and the phototropic semicarbazones and hydrazones therefore have the *trans* form with reference to the C=N bond.[35f] Colorless benzylidenebromopyruvic acid (PhCH=CBrCOCOOH) in benzene becomes yellow in diffuse light, and on exposure to sunlight in thin layers the color fades; the yellow intermediate compound is probably a geometrical isomer of the original acid, and the colorless substance produced by exposure to sunlight is a dimer.[35g] A primary phototropic change may be accompanied or followed by an irreversible chemical change; thus Singh and Bhaduri[35h] observed that the colorless solution of α-naphthylaminocamphor in chloroform turned green on exposure to sunlight; simultaneously there was a photochemical oxidation to α-naphthyliminocamphor. It was suggested that the phototropic change involved a reaction with chloroform resulting in the formation of a triphenylmethane dye; the explanation was based on the analogy of the color changes of phototropic triphenylmethane dyes.[35i] The phototropic change of phenyliminocamphors is considered to be not due to polymerization and depolymerization since there is no change in magnetic susceptibility.[35j] Bhatnagar, Kapur, and Hashmi examined the magnetic properties of phototropic compounds, and concluded that cinnamylidenemalonic acid underwent polymerization and *o*-nitrobenzaldehyde isomerization.[35k] Acetanilide *p*-disulfoxide is phototropic, but only in the presence of about 0.1% of the corresponding disulfide; this observation indicates the possibility of reduction as a prelude to the phototropic change.[35l]

A possible connection between phototropy and the more general, irreversible phenomenon of fading is indicated by the observation that some phototropic changes are initiated or accelerated by oxygen. Thus it is only in presence of oxygen that colorless benzaldehyde phenylhydrazone undergoes a phototropic change to orange-yellow and then to red.[36] The color changes are accompanied by the formation of $(PhCH{=}N{-}NPh)_2$, benzaldehyde and benzoic acid. The phototropy of diacetyl derivatives of 4,4′-diaminostilbene-2,2′-disulfonic acid and its salts is accelerated by oxygen.[36]

Constitution of Dyes and Light Fastness

The photochemistry of simple organic compounds (e.g., aldehydes, ketones, saturated and unsaturated aliphatic acids) has been extensively investigated; photo-products have been isolated and the formation of free radicals has been demonstrated; the kinetics of the reactions have been studied and quantum efficiencies have been determined. Dealing with dyes of relatively complex character, it has been possible only in very few instances to isolate and identify the photo-products. Some of the difficulties are that photochemical processes in dyes are very slow and the quantum efficiencies very small fractions. When decomposition products are isolated, the problem is to distinguish the primary or photochemical change from the subsequent thermal and other reactions, and formulate the mechanism by which the ultimate degradation products are formed.

Gebhard[37] was perhaps the first to attempt a correlation of the chemical constitution of dyes with their fastness to light. He found that hydroxyl and amino groups accelerated fading, and alkylation of the amino groups accelerated it further. Chlorine and bromine atoms, the sulfonic group and the carboxyl group retarded fading, the last most powerfully. The position of the substituent is also important. Among the alizarin dyes, Gebhard found that the fastness to light depended on the number, nature and position of the substituent groups; in addition to the hydroxyl and amino groups, thiol groups and the quinoline ring increased fading, while the nitro group decreased it. From the extensive data now available, it is clear that fastness to light is a complicated phenomenon and cannot be related to the invariable effects of specific groups. Thus halogenation among the indigoids and anthraquinonoid vat dyes usually increases light fastness; but both among these and other classes of dyes, halogen may be ineffective or even decrease the light fastness. The sulfonic group often favors light fastness, but a notable exception is the much greater fastness of azoic shades in comparison with the direct cotton dyes in general.

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[36] Stobbe *et al.*, *Ber.* **46,** 1226; 2887 (1913).

[37] Gebhard, *J. Soc. Dyers Colourists* **25,** 305 (1909).

Nitro dyes. Nitro dyes appear to fade by reduction to azoxy and azo compounds[38] and ultimately to primary amines. Naphthol Yellow S fades by photoreduction to 2-nitro-4-amino-1-naphthol-7-sulfonic acid.[39] A photochemical reaction, which may have a bearing on the behavior of dyes containing nitro and sulfonic groups towards light, is the transformation of 1-nitronaphthalene-8-sulfonic acid in aqueous solution to 1′-nitro-1-amino-2-hydroxy-8,8′-dinaphthylsulfone.[40]

Azo dyes. Azo dyes vary in light fastness within wider limits than dyes of any other class. This is to be expected, since the azo dyes are a very numerous class including types which differ in the number of the azo groups, the character of the ring systems which the azo groups unite, and the number and nature of the auxochromes. The light fastness of various types of azo dyes and the structural factors which are favorable to light fastness have been reviewed in Chapter XI.[41] A primary amino group leads to low light fastness, and acylation (especially with a chlorinated acid) increases the fastness. Specific groups such as the $-SO_2R$, $-SO_2NR_2$, $-OSO_2Ar$, CF_3 and alkoxy groups may be introduced for the purpose of increasing the light fastness. Phenyl-peri-acid, γ-acid (acid-coupled) and 5-pyrazolones as coupling components often yield wool dyes with good light fastness. The yellows and oranges among the direct cotton dyes have in general a higher level of light fastness than the blues and greens. The benzidine type of direct cotton dye usually has poor light fastness. Among the yellow, orange and brown stilbene dyes, and red, violet, blue and green disazo and trisazo dyes of the type ($A \rightarrow M^1 \rightarrow M^2 \rightarrow E$) in which E is J-acid or an *N*-substituted derivative, good fastness (5–6 and as much as 7 for a few stilbene dyes) has been attained. Azoic shades produced from the Naphtol AS series are of a generally higher level of fastness than the direct cotton dyes. The average light fastness of the technically used azoic combinations is about 5, and some reach a grade of 6–7.[41a] The position of nuclear substituents in some simple azo dyes can be correlated with their fastness to light and washing; β-naphthol derivatives are faster than the α-naphthol analogs; among the three aniline sulfonic acids, orthanilic acid yields the fastest azo dyes.[42]

Exposed to light on cotton or in solution, 1-*p*-sulfobenzeneazo-*N*-phenyl-2-naphthylamine (I) gives the triazolium salt (II) and naphthophenazine (III) in 44 and 16% yield respectively;[43] (II) is the primary oxidation product, formed from (I) by dehydrogenation and reverts to (I) by reduction. The phenazine (III) is probably formed from (II) by the further action of light. The changes also occur in the absence of oxygen (although much more slowly), so that the oxidizing agent must be the dye itself. The stability of azo dyes from *N*-alkyl-β-naphthylamines is much greater and they are not so readily convertible into triazolium salts.

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[38] Mounier, *Tiba* **9,** 5, 121, 237, 353, 469, 585 (1931).

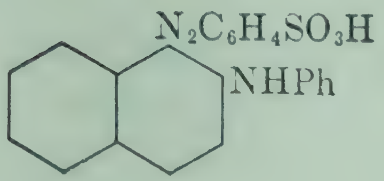
[39] Hodgson and Smith, *J. Soc. Chem. Ind.* **56,** 108T (1937).

[40] Voroshcov and Kozlov, *J. Gen. Chem. U.S.S.R.* **7,** 1610 (1937).

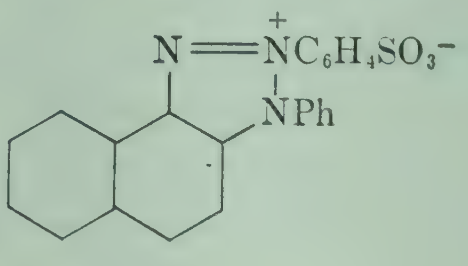
[41] See also Chapters XII-XXII.

[41a] See also Pinte and Millet, *Bull. inst. textile France,* No. 9, 29 (**1949**).

[42] Brode and Griffith, *Ohio Agr. Expt. Sta. Bull.* No. 565 (**1936**).



(I)



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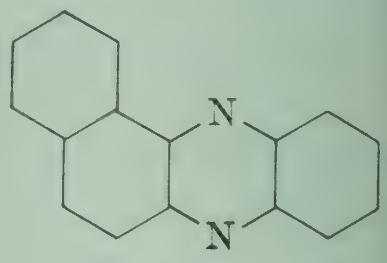

(III)

Fading of azo dyes is an oxidation process. The photochemical oxidation of cellulose is accompanied by evolution of carbon dioxide, and cotton dyed with simple azo dyes yields more carbon dioxide on illumination than undyed cotton.[23, 38] Haller and Ziersch observed the formation of 1,2-naphthoquinone, phthalic and phthalonic acids, when cotton dyed with azo dyes from β-naphthol was exposed to the light of an arc. Oxidation of such azo dyes in aqueous solution with hydrogen peroxide and other oxidizing agents breaks the N=N bond, and color reactions of exposed dyed samples indicate a similar fission on the fiber.[23, 43a] When calico dyed with Chlorazol Sky Blue and other direct azo dyes is exposed to sunlight, complete destruction of the dyes occurs long before the cellulose exhibits marked reducing action; the fading action is apparently not the result of reduction by cellulose under the influence of light,[44] but further investigation including the estimation of the carboxyl content of the cellulose after exposure is necessary. Atherton and Selzer have found that the destruction efficiencies for a series of dyes (aniline or substituted aniline → α-naphthylamine) in cellulose acetate film, on exposure to light from a carbon arc, are in the reverse order to the dissociation constants of the corresponding substituted benzoic acids. Assuming that the initial step in the fading reaction is the formation of an azoxy compound, and that Hammett's rule connecting the effect of *m*- and *p*-substitution in benzene derivatives on reaction rates can be applied to photosensitized processes, they explain the observed relationship on the basis of the electrophilic character of the substituents.[4a]

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[43] Krollpfeiffer, Muhlhausen, and Wolf, *Ann.* **508,** 39 (1933).

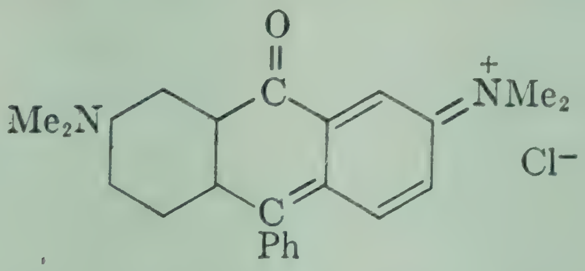
[43a] Desai and Giles, Symposium on Photochemistry in relation to textiles, *J. Soc. Dyers Colourists* **65,** 585 (1949).

[44] Hibbert, *J. Soc. Dyers Colourists* **43,** 292 (1927); contrast Harrison, *ibid.* **30,** 206 (1914).

Blaisdell has recently demonstrated the reduction of an azo group by irradiation in presence of a hydrogen donor. The action of light on solutions of azobenzene in isopropyl alcohol and isooctane results in the addition of hydrogen extracted from the solvent; hydrazobenzene, and later aniline, is formed. In the presence of oxygen there is a photosensitized oxidation of the solvent.[4a]

The fastness of many azo dyes is improved by an aftertreatment with copper salts on the fiber. The copper complexes of the dyes may be prepared in substance, and some direct cotton dyes of this type have excellent fastness to light.[45] Phenyl disodium phosphate and similar aryl derivatives of the acids of phosphorus have been claimed to improve the light fastness of direct dyes on cotton.[46]

Basic dyes. Basic colors as a class are very fugitive to light; the fastness grade is mostly the lowest (1), and for a few dyes 1–2. The ammonium, oxonium and sulfonium groups, which impart basic dyeing properties, appear to be responsible for the photosensitivity. So long as these are present, the fading of the dye by the action of light can only be altered to a minor degree by varying the other parts of the dye molecule. Acid and vat dyes derived from anthraquinone and anthrone usually have good fastness to light; the anthrone derivative (IV) dyes wool, silk and tannin-mordanted cotton bright green shades which are fast to acids, alkalis, and washing, but fugitive to light, being only very slightly faster than Malachite Green in this respect.[47] When sulfonic groups are introduced into basic triphenylmethane dyes, the acid dyes on wool and silk have higher light fastness than the basic dyes on tannin-mordanted cotton. The difference is usually small, but certain acid triarylmethane dyes (e.g., indole derivatives and dyes containing *p*-alkoxyanilino groups) have good light fastness. Among the Rhodamines, which are derivatives of triphenylmethane and also of xanthene, dyes of the Fast Acid Violet ARR type (sulfonic acids of *N*-phenylrhodamines)



(IV)

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[45] See Chapters XIII and XVII.

[46] Ciba, BP 543,575.

[47] Jones and Mason, *JCS* 1813 (**1934**).

reach a light fastness grade of 5. The Wool Fast Blues of the azine class have light fastness 4–5. While the basic oxazine dyes have very poor light fastness as usual, there are direct cotton dyes of the dioxazine type which have excellent light fastness (6–7).

When a dye which has excellent fastness and contains a trivalent nitrogen atom is converted into an ammonium salt, the light fastness is invariably decreased. The treatment of a direct dye on cotton with ammonium salts containing paraffin chains for the purpose of improving the washing fastness generally lowers the light fastness, and it has been shown that the effect is not due to the aliphatic groups, but to the formation of an ammonium salt of the cationic reagent and the dye anion. Cationic softeners have a similar effect and it has been suggested that the softening of dyed textiles is preferably carried out with anionic reagents such as the alkali salts of the complex amides formed by the condensation of fatty acids with polyethylenepolyamines or the alkali salts of the products obtained by heating such amides with urea.[48]

Many cationic dyes are oxidants and under light excitation contain enough energy to effect various oxidations such as ferrous to ferric ions.[49] When a solution of Methylene Blue and ferrous sulfate is irradiated, the leuco derivative of the dye is formed; the reaction is reversible, and in the dark the ferric salt regenerates Methylene Blue.[50] The fading of such a dye can be the result of autoxidation or of oxidation by hydrogen peroxide formed by the photosensitized autoxidation of water (see later).

By the action of light on basic dyes in the absence of air or other oxidizing agent, the leuco derivatives are formed.[51] The oxalates of Malachite Green and Crystal Violet are converted into *p*-dimethylaminobenzophenone and Michler's ketone respectively by the action of light and air.[51, 25] The addition of hydrogen peroxide to the aqueous solution greatly accelerates the reaction. Studying the kinetics of the reaction for a few triphenylmethane dyes, Vaidya, Desai, and Khanderia[52] found that the change was in general proportional to the time of exposure, while the decomposition of nitro and azo dyes was proportional to the square root of time with a considerable period of induction. Photochemical change to the same extent was effected by absorption of light energy by solutions of Brilliant Green in the three main regions of absorption (6450–5700A; 4400–4180A; 3220–3100A) in the ratio 1.5:1:1, so that the quantum efficiency in the region of the first absorption band was about 33% lower than in the blue-violet and ultraviolet regions, assuming the reaction to be of the first order. A characteristic of the fading process for three of the four triphenylmethane dyes examined (Magenta, Methyl Violet, Brilliant Green) was the very low quantum efficiency (5–11 molecules per million quanta of the light energy absorbed); ϕ was higher (52–59) for Methyl Green which has two cationic charges. There was a decrease in the quantum efficiency with increasing concentration of the aqueous solution, apparently due to collisional deactivation as in the quenching of the fluorescence of solutions of Eosine and other fluorescent dyes by increasing the concentration above certain limits.

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[48] McLeod, *Am. Dyestuff Reptr.* **37,** 30 (1948); USP 2,344,259–60.

[49] Rabinovitch, Photosynthesis, Vol. I, Interscience, New York, 1945.

[50] Weiss, *Nature* **136,** 794 (1935); **138,** 80 (1936); *Trans. Faraday Soc.* **35,** 48 (1939).

[51] Iwamoto, *Bull. Chem. Soc. Japan* **10,** 420 (1935).

[52] Private communication.

A remarkable instance of demethylation is the action of ultraviolet light on a solution of Crystal Violet, when fuchsine is formed, besides colorless compounds resulting from more profound degradation.[53]

The leuco bases of the triphenylmethane dyes (e.g., Malachite Green and Crystal Violet) are extremely light-sensitive; they are converted into the colored quinonoid compounds. An application of these dyes in actinometry depends on the behavior of the leuco cyanides which are colorless in the dark, and become colored on irradiation, as a result of photoionization.[54]

While the tannin-antimony lakes of basic dyes have low light fastness, lakes with phosphotungstic, phosphomolybdic and especially phosphomolybdotungstic acids have greatly improved fastness to light, and they are valuable pigments.[47] The light fastness of basic dyes on tannin-antimony mordanted cotton can be increased substantially (from grade 1–2 to 3–5) by aftertreatment with phosphomolybdotungstic acid (e.g. Auxanine B, IG). The light fastness of Astraphloxine FF can be raised from 1 to 5–6 by this treatment. The light fastness of lakes of triphenylmethane dyes with molybdic and other complex inorganic acids increases, up to a certain maximum, proportionately to the amount of acid adsorbed on the lake in excess of that required for salt formation.[55] This effect has been ascribed to the presence of the adsorbed acid on the surface of the color lake particles; bleaching of the color lake as a result of light absorption is then prevented by the screening action of the inorganic substance. The increased stability to light may be at least partly due to the intrinsic properties of the color lake as a substance chemically distinct from the parent dye. Bancroft and Ackerman suggest that the higher light fastness results from a lowering of the chemical potential to an extent dependent on the affinity of the dye for the substrate.[15]

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[53] Henriquez, *Rec. trav. chim.* **52,** 991 (1933).

[54] Lifschitz, *Ber.* **52,** 1919 (1919), *et seq.*; Harris *et al.*, *JACS* **57,** 1151 (1935).

[55] Neergaard, *Kemisk* **21,** 77 (1940); *Ingeniøren,* **50,** No. 73, K81; No. 86, K115; **51,** No. 4, K1 (1942).

When a trimethylammonium or similar group is introduced into the 7- or 8-position of 1-nitroso-2-naphthol, the green iron complexes dye as basic dyes on tannin-mordanted cotton, and the shades have good fastness to light.[56]

While it is generally accepted that the chemical action of light is dependent on the quantum absorbed, and therefore on the frequency of the light, Rein has attempted to relate the increase in fastness to light of basic dyes when they are converted into the phosphotungstates, and the similar behavior of azo dyes when they are converted into copper complexes, to lowering of the intensity of absorption.[56a]

Indigoids. On wool indigo and the halogenated indigos have excellent light fastness (8), and a grade of 6–8 is attained by many indigoid and thioindigoid dyes on the protein fiber. On cotton indigo and other indigoid dyes usually have light fastness only of the grade 3–4; but a few magenta and pink thioindigoid dyes have higher fastness (5–6). When indigo-dyed cotton is exposed to light, slow fading occurs and ultimately the shade becomes yellow; at this stage accelerated photochemical oxidation of cellulose takes place.[57] Isatin has been isolated from the products of the photochemical degradation of indigo;[44] this is one of the few examples in which the fading of a dye has given an isolable decomposition product. From Ciba Blue 2B dyed on cotton, dibromoisatin has been isolated in a yield of about 3%.[58]

Indigo white and then indigo are formed when the halogenated indigos in aqueous caustic soda-hydrosulfite solution are exposed to sunlight in a sealed tube;[59] this is an example of the dehalogenations effected by the action of light and is not confined to the indigoid series. With halogenated dyes of both the anthraquinone and indigoid series, the dyed materials are off shade if, after impregnation in the vat, there is exposure to sunlight before oxidation, and the effect is due to dehalogenation.[60] When 1- and 2-chloroanthraquinones are reduced in alkaline solution to the anthrahydroquinones, and exposed to white light, they are dehalogenated.[61]

Anthraquinone derivatives. Sulfonic acids of aminoanthraquinone derivatives as wool dyes and the anthraquinonoid vat dyes for cotton are among the fastest dyes in the entire range of synthetic dyes. A light fastness grade of 6–7 for the acid anthraquinone dyes and of 6–8 for the vats is the general level. As dispersed dyes for cellulose acetate, the aminoanthraquinones and their derivatives are somewhat lower in the scale. It has been mentioned earlier that many vat dyes on nylon have much lower light fastness than they have on cotton. Blaisdell has suggested that the difference is mainly due to the existence of the dyes as relatively large crystals in the cotton fiber, while their growth in the denser hydrophobic nylon fiber is greatly retarded.[4a]

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[56] Geigy, BP 305,648.

[56a] *Z. angew. Chem.* **47,** 159 (1934).

[57] Haller *et al.*, *Melliand Textilber.* **9,** 415 (1928).

[58] Scholefield, Hibbert and Patel, *J. Soc. Dyers Colourists* **44,** 236 (1928).

[59] van Alphen, *Rec. trav. chim.* **63,** 95 (1944).

[60] Weber, *Am. Dyestuff Reptr.* **22,** 157 (1933).

[61] Goldstein and Gardner, *JACS* **56,** 2130 (1934).

Sulfur dyes. The light fastness varies from 3–4 for the yellows and browns to 5–6 for the blues and greens and 7 for the blacks. The fastness of the yellows and browns can be increased considerably by after-treatment with copper (and to a less extent with chromium) salts. Metal complexes are probably formed, but unlike the coordination complexes of the azo dyes which are well characterized and have been prepared in substance for subsequent application in dyeing, the products of the action of copper and chromium salts on sulfur dyes have not been investigated.

Light fastness of pigments. The fading of pigments used in paints, varnishes and other decorative coatings is in some ways even more difficult to assess and interpret than the fading of dyed fabrics, since the materials (vehicles, extenders, etc.) in conjunction with which pigments are used are many and varied.

Broad correlations have been noticed regarding the chemical constitution of organic pigments and their stability to light.[62] The highest degree of fastness is shown by the phthalocyanines and other metallic complexes. Copper and iron are especially effective in imparting light fastness. Combination of the fugitive basic and acid triphenylmethane dyes with the complex acids of phosphorus, molybdenum and tungsten yields lakes with excellent fastness to light. Among the azo dyes, laking with barium and calcium improves light fastness.[63] The titanium-precipitated derivatives, particularly those made from the glycerochloride of titanium, are superior to the corresponding barium derivatives of sulfonated acid dyes in their fastness to light, and they have also greater color strength and softer texture.[64] In a series of closely related azo dyes it is found that chlorine atoms and nitro groups are favorable to light fastness. The azoic pigments from the anilides of 2-hydroxy-3-naphthoic acid have better fastness than the β-naphthol analogs.[65]

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[62] Mackenzie-Richards, *J. Oil & Colour Chemists' Assoc.* **22,** 262 (1939).

[63] C. D. Allen, Red Organic Pigments in Mattiello's Protective and Decorative Coatings, Vol. II, Wiley, New York, 1942.

[64] Hancock and Stevens, *J. Oil & Colour Chemists' Assoc.* **24,** 293 (1941).

[65] Walker, *J. Oil & Colour Chemists' Assoc.* **30,** 91 (1947).

DEGRADATION OF CELLULOSE DYED WITH CERTAIN YELLOW AND ORANGE VAT DYES

The photosensitizing action of pigments and dyes of certain types, such as chlorophyll and the cyanines, has been known for a long time, and is a technically valuable property used in photographic processes.[66] The ability of some dyes to accelerate chemical reactions induced by light becomes an unpleasant trait when they manifest such activity on fibers. Accelerated tendering of cellulose in this manner has been observed with a variety of dyes (e.g., Auramine and other basic dyes, some sulfur and azoic dyes),[23] but anthraquinonoid vat dyes have received particular attention because of their own fastness to light.

Examples of active vat dyes. When cellulose is exposed to light,[67] degradation takes place very gradually, and the change can be followed by observations of the loss of tensile strength and increase in (a) reducing power (copper number), (b) fluidity of cuprammonium solutions, (c) alkali solubility, and (d) Methylene Blue absorption. After prolonged exposure, the fibers become completely brittle and fall to a powder. The formation of oxycellulose and humic substances is accompanied by the evolution of carbon monoxide and dioxide. The photochemical "tendering" of cellulose is accelerated when it is dyed with certain dyes, mainly yellow and orange vat dyes of the anthraquinone series.[68–70] Such catalytic activity is a serious defect, for dyes which may be satisfactory from other points of view, including their fastness to light, are then valueless for dyeing and printing fabrics, such as curtain materials, liable to be exposed to direct sunlight for long periods. Two examples of severe tenderers in the commercial range of vat dyes are Indanthrene Yellow FFRK and Indanthrene Golden Yellow GK, both of which have very good light fastness (6–7); the former has excellent fastness to all other agencies, while Golden Yellow GK is deficient only in its fastness to alkali boil. Cibanone Orange R, which was withdrawn from the commercial range because of its tendering activity, has a light fastness of 6–7. In general, however, marked degradation of the cellulose substrate is accompanied by fading of the dye. It was a startling discovery when the light-tendering action of well-known anthraquinonoid dyes was recognized, for the cotton industry had come to depend on these vat dyes as a class for outstanding fastness, especially to light. The practical aspects of the phenomenon have therefore been widely studied by dye manufacturers and users,[71,71a] as a result of which the "safe" dyes have been classified and distinguished from the "dangerous" dyes and from those which are on the borderline. Dyes in the latter category are regarded with suspicion and are used only for materials not likely to undergo prolonged exposure to light. Yellow and orange vat dyes, absorbing strongly in the region 3600–4000A, are the most active tenderers; red, brown, violet and bordeaux dyes are less active; blue, green, and black dyes are inactive so far as tendering by light action is concerned. Attempts have been made, though on insufficient data, to correlate "the extent of destructive action with the completeness of absorption" in the 3600–4000A region of the spectrum.[72] All the yellow and orange anthraquinonoid dyes are not tenderers, indicating that other characteristics besides color are involved. Studying the behavior of a large number of vat dyes, Landolt[73] found that 75% of the yellows and oranges, 50% of the scarlets and reds, 30% of the violets, but none of the blues and greens are capable of accelerating the degradation of cellulose by light. The yellows and oranges, however, are far more powerful in their tendering action than the scarlets, reds and violets. When an active dye is present on the fiber in admixture with a second and inactive dye, the action of light on the dyed cellulose is dependent on the potency of the active dye as a tenderer and on the light fastness of the second dye; the light-fast direct cotton color, Chlorantine Light Blue 4GL, has been found to diminish the degradation of cellulose.[73] The light fastness of the second dye (e.g., a blue vat dye) may be considerably reduced. Thus both the active Anthra Yellow GC (Caledon Yellow 5G) and the inactive Ciba Blue 2B have good light fastness (about 5); but when cotton is dyed with a mixture of the two and exposed to light, the blue dye fades rapidly until it is completely destroyed. The decomposition product is yellow in color, so that the original green shade of the mixed dyeing turns into yellow; and when the blue dye is no longer available for the light-activated Anthra Yellow molecules to act upon, the energy is transmitted to the cellulose substrate which then undergoes oxidation.[68] Cibanone Orange R promotes rapid decomposition of Direct Sky Blue when dyed in admixture with it.[74] The powerful tenderer Hydron Yellow NF (Indanthrene Yellow GF) degrades not merely the cotton warp, dyed with this

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[66] See Chapter XXXVIII.

[67] For a review, see Appleby, *Am. Dyestuff Reptr.* **38,** 149 (1949).

[68] Haller, *Melliand Textilber.* **5,** 541 (1924).

[69] Scholefield and Patel, *J. Soc. Dyers Colourists* **44,** 268 (1928).

[70] For a review, see Turner, *J. Soc. Dyers Colourists* **63,** 372 (1947).

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[71] Whittaker, *J. Soc. Dyers Colourists* **49,** 9 (1933); **51,** 117 (1935); *J. Soc. Chem. Ind.* **52,** 140T (1933).

[71a] See also Fox, *J. Soc. Dyers Colourists* **65,** 528 (1949).

[72] Scholefield and Goodyear, *Melliand Textilber.* **10,** 867 (1929).

[73] *Melliand Textilber.* **14,** 32 (1933).

[74] Landolt, *Melliand Textilber.* **11,** 937 (1930).

dye, in a cotton-viscose union fabric, but also those parts of the blue vat-dyed viscose weft which are in close contact with the tendered warp.[75] Landolt has drawn up a list of safe dyes, and has also shown that even the dangerous dyes can be used in carefully chosen mixtures. Active vat yellows are only deleterious in mixtures with fast blues after a certain minimum proportion of the yellow has been exceeded.[76] In this connection it is interesting to note that high fastness to light has been specially claimed for the yellowish green dyeings produced by a mixture of dimethoxydibenzanthrone (Caledon Jade Green) and the highly active Indanthrene Yellow 3GF type of dye.[77] Some of the dangerous dyes, in addition to those mentioned earlier, are Cibanone Yellow R, Indanthrene Yellow 5GK and Indanthrene Golden Orange G. Yellow and orange vat dyes free from the tendering defect are now available for dyeing, but some of the active dyes continue to be used for calico printing because of their suitability for the printing process.

Factors affecting light-tendering activity. With a given vat dye possessing tendering activity, cotton and viscose are about equally susceptible, although conflicting statements have been made regarding their relative resistance and their suitability as materials for casement curtains.[71] Silk is more readily attacked than the cellulose fibers, and wool is the most resistant, being unaffected for all practical purposes.[73] The relative susceptibility of various fibers to the light-tendering action of vat dyes therefore runs parallel to their behavior towards light. The activity of the same vat dye on cotton, viscose, silk and nylon depends on the humidity of the air; in moisture-saturated air, the degradation is in the following decreasing order: silk, nylon, cotton, and viscose.[78] Many of the dyes which increase the photochemical degradation of nylon are least fast to light on this fiber.[79]

For a given dye, the degree of degradation of the cellulose substrate increases with increasing depth of shade and longer time of exposure. Open weave fabrics and fabrics constructed from dyed yarn undergo degradation more rapidly than tightly woven and piece-dyed material, the determining factor being the accessibility of the dye to light. Atmospheric humidity has a profound influence on the degradation of cellulose by light in presence of the active vat dyes, as shown by Egerton's data (Table I)[80] on the increase in cuprammonium fluidities of undyed cotton

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[75] Ermen and Goodyear, *Textile Mfr.* **55,** 437 (1929).

[76] Fitzsimmons, *J. Soc. Dyers Colourists* **50,** 305 (1934).

[77] General Aniline and Film, USP 2,227,834.

[78] Egerton, *J. Textile Inst.* **39,** T293 (1948). See also Ref. 4a.

[79] Egerton, *J. Soc. Dyers Colourists* **64,** 336 (1948).

[80] Egerton, *J. Soc. Dyers Colourists* **63,** 161 (1947). See also Ashton, Clibbens, and Probert in Ref. 4*a*.

TABLE I

(Egerton)

INCREASE IN FLUIDITY OF DYED AND UNDYED COTTON EXPOSED TO SUNLIGHT (5,000 MICROWATT-HOURS PER SQ. CM.) IN DRY AND HUMID AIR

		Fluidity	
No.	*Dye*	0% R.H.	100% R.H.
1.	Caledon Brilliant Blue R	3	3
2.	Caledon Jade Green G	4	4
3.	Ciba Green G	4	6
4.	Indanthrene Khaki 2G	5	7
5.	Indanthrene Brown BR	5.5	7
6.	Caledon Red BN	9	12
7.	Durindone Blue 4B	4	13
8.	Indanthrene Brilliant Orange GR	10	14
9.	Undyed (bleached) cotton	3	15
10.	Caledon Red 5G	6	15
11.	Caledon Red X5B	6	15
12.	Indanthrene Pink FBBL	7	15
13.	Indanthrene Orange 6RTK	12	16
14.	Caledon Red 2G	6	17
15.	Indanthrene Gold Orange 3G	15	17
16.	Indanthrene Brilliant Orange RK	11	19
17.	Algol Yellow WG	5	23
18.	Indanthrene Yellow 3RT	12	24
19.	Indanthrene Orange RRK	16	24
20.	Indanthrene Brilliant Orange GK	15	25
21.	Cibanone Orange 6R	16	25
22.	Caledon Orange 2RT	17	25
23.	Caledon Yellow 3G	8	26
24.	Indanthrene Yellow 3GF	13	26
25.	Caledon Yellow G	16	26
26.	Indanthrene Yellow 7GK	10	27
27.	Indanthrene Golden Yellow RK	14	28
28.	Durindone Scarlet Y	10	29
29.	Caledon Orange 4R	16	30
30.	Caledon Gold Orange G	18	30
31.	Indanthrene Yellow 5GK	19	33
32.	Cibanone Orange R	20	38
33.	Indanthrene Yellow FFRK	16	39
34.	Indanthrene Yellow GF	19	39
35.	Indanthrene Printing Yellow GOK	13	41
36.	Caledon Yellow 5G	18	46
37.	Cibanone Yellow R	19	52

and of cotton dyed with a series of vat dyes on exposure to light in dry air and at 100% RH.

Moisture has practically no effect on the photochemical oxidation of cellulose in presence of inactive dyes such as the blues and greens; the effect is less than in the case of undyed cotton. Flavanthrone (Caledon Yellow G) and Indanthrene Yellow 7GK have considerable activity as light-tenderers in a humid atmosphere, according to Table I, but Flavanthrone is usually classified among the relatively safe dyes and special claims have been made for Indanthrene Yellow 7GK as a nontenderer. Egerton's work is valuable because it provides quantitative data for a comparison of the light-tendering action of a series of vat dyes examined under a standard set of conditions. There is need, in fact, for more extensive data on the full commercial range of yellow, orange, and red dyes, and for the planning and interpretation of the exposure experiments on a statistical basis in order to avoid conclusions being drawn from adventitious results. Egerton and others have usually employed commercial brands of dyes and this is probably one of several reasons for the differences in the results recorded by various workers, for instance in Tables I, II, III, and V. Pure dyes have to be used for studying the relation between their chemical constitution and photochemical activity.

Fox has examined the behavior of 34 commercial vat yellows and oranges, when dyed in a medium depth of shade on bleached cotton fabric and exposed to sunlight and the industrial atmosphere of Huddersfield; his results are recorded in Table II.[71a]

Landolt has made a quantitative comparison of the photochemical activity of simple anthraquinone derivatives, anthraquinonoid vat dyes and thioindigoids by topping the dyeings on cotton with 0.2% Direct Sky Blue GS, exposing to light under standard conditions, and determining the difference in reflectance between the unexposed and exposed dyeings.[4a] The results, stated as "blue test %", are recorded in Table III.

Exposure in an atmosphere of carbon dioxide or nitrogen leads to a very small rise in cuprammonium fluidity (Table IV), which may be due to the difficulty of completely removing oxygen from the system.[80]

Vat-dyed mildly alkaline cotton is markedly inferior in light fastness to neutral or mildly acid cotton.[13] A favorable factor of great potency for the degradation of cellulose is high alkalinity in the dyed cellulose under exposure, and still greater tendering activity results if the dye on the fiber is partially or completely in the leuco condition. In the procedure for examining the activity of a dye, prolonged exposure to light under neutral conditions can be usually replaced by short exposure under alkaline conditions, since comparable results are obtained; but there are exceptions (e.g., Indanthrene Orange 6RTK and Helindone Yellow 3GN).

TABLE II
(Fox)

Dye	*Light fastness*
A—Highly Active	
Anthraflavone G	3
Cibanone Yellow R	4
Paradone Yellow GC	4–5
A-B—Active	
Algol Yellow 8G	4
Cibanone Orange R	6–7
Cibanone Yellow 2GR	5
Sandothrene Orange N4G	6
Indanthrene Yellow 6GD	4–5
Indanthrene Yellow GF	5
Indanthrene Golden Yellow GK	5–6
Indanthrene Gold Orange G	5–6
Indanthrene Yellow 5GK	5–6
Indanthrene Yellow FFRK	6–7
Cibanone Orange 2R	5
B—Moderately Active	
Cibanone Gold Orange 2G	5
Indanthrene Yellow GK	6
Indanthrene Brilliant Orange GK	7
Indanthrene Brilliant Orange RK	7–8
Indanthrene Yellow 7GK	5–6
Indanthrene Yellow 4GK	7
C—Mildly Active (Border Cases)	
Caledon Yellow 4GS	5–6
Indanthrene Orange RRT	6
Indanthrene Golden Yellow RK	7
Cibanone Orange 6R	6
Indanthrene Brilliant Orange GR	6–7
Indanthrene Orange 4R	6–7
D—Inactive	
Indanthrene Yellow 3RT	7–8
Caledon Yellow 2RS	7
Caledon Yellow 5RS	6
Indanthrene Yellow 3GF	5
Paradone Yellow G New	6
Caledon Gold Orange 3G	7
E—Protective	
Indanthrene Orange GG	7–8
Indanthrene Orange RR	7

TABLE III
(Landolt)

Dye	*Shade*	*Blue test %*
Anthraquinone	Colorless	1
1-Aminoanthraquinone	Brown	0
1,5-Diaminoanthraquinone	Red-brown	0.5
1-Benzamidoanthraquinone	Sulfur yellow	0
1,5-Bisacetamidoanthraquinone	Pale yellow	0
1,5-Bisbenzamidoanthraquinone	Sulfur yellow	2.5
1,5-Bis-*p*-chlorobenzamidoanthraquinone	Yellow	9
1,5-Bis-*o*-chlorobenzamidoanthraquinone	Pale yellow	0
1,5-Bis-*p*-aminobenzamidoanthraquinone	Brown	1
1,5-Bis-*p*-dimethylaminobenzamidoanthraquinone	Brown	3
1,5-Bis-*p*-methoxybenzamidoanthraquinone	Reddish yellow	5.5
1,5-Bis-β-naphthamidoanthraquinone	Pale yellow	3
1,5-Bisnicotinamidoanthraquinone	Yellow	0.5
1,5-Bisbenzamido-4,8-dihydroxyanthraquinone	Violet-blue	1.5
Flavanthrone	Yellow	0.5
Dibenzopyrenequinone	Yellow	7
Dibromodibenzopyrenequinone	Golden yellow	6
Pyranthrone	Yellow-orange	10
Bromopyranthrone	Orange	8
Dibromoanthanthrone	Red-orange	6.5
Dichloroanthanthrone	Orange	7
Tribromopyranthrone	Red-orange	6
Anthanthrone	Brown-orange	1.5
Carbazolized 5,5′-bisbenzamido-1,1′-dianthrimide	Reddish yellow	5
Carbazolized 1′,1″,1,5-trianthrimide	Reddish yellow	3.5
Carbazolized 1′,1″,1,4-trianthrimide	Reddish brown	2
Carbazolized 5-benzamido-1′,1″,1,4-trianthrimide	Yellow-brown	0
Carbazolized 8′,8″-bisbenzamido-1′,1″,1,4-trianthrimide	Red-brown	0.5
Carbazolized 4,5′-bisbenzamido-1,1′-dianthrimide	Orange-brown	2
Carbazolized 4,4′-bisbenzamido-1,1′-dianthrimide	Olive	1
Carbazolized 1′,1″,1‴,1⁗,1,4,5,8-pentanthrimide	Yellow-olive	0
Thioindigo	Blue red	0
6,6′-Diethoxythioindigo	Orange	6
6,6′-Dichlorothioindigo	Blue-red	3
5,5′-Dichloro-7,7′-dimethylthioindigo	Red-violet	2
6,6′-Dichloro-4,4′-dimethylthioindigo	Red	4.5
5,7,6′-Trichloro-4,6,4′-trimethylthioindigo	Pink	5
5,5′-Dichloro-4,7,4′,7′-tetramethylthioindigo	Red-violet	5

TABLE IV
(Egerton)
DYED AND UNDYED COTTON EXPOSED IN VARIOUS GASES TO A H. P. MERCURY LAMP (250 WATTS)

Atmosphere	*% R.H.*	*Time of exposure (hours)*	*Fluidity rise*		
			Cibanone Yellow R	*Ciba Yellow G*	*Undyed cotton*
Carbon dioxide	0	70	2.6	0.3	0.7
Nitrogen			2.7	0.8	1.4
Air			16.9	14.9	4.5
Oxygen			28.6	20.8	4.8
Carbon dioxide	100	45	3.0	0.7	0.9
Air			29.0	11.2	7.7

which are dangerous on long normal exposure, but do not tender by short exposure of the dyed cellulose in presence of alkali.[73]

Scholefield and Patel have studied the action of light on cellulose during the dyeing process.[69, 81] If light is allowed to act on cotton saturated with the leuco compounds of certain yellow and orange vat dyes, tendering occurs. With some dyes the action of light at such a stage is to change the hue and in rare cases to destroy the dyestuff completely. Tendering by the action of light during dyeing may be prevented by the use of ⅛% of sulfite cellulose waste liquor or tannic acid in the dyebath.[71, 82] If sunlight is allowed to fall on cotton dyed with yellow or orange vat dyes and saturated with a dilute alkaline solution of hydrogen peroxide, the oxidizing action of the dye-hydrogen peroxide system may produce one or more of the following effects: (1) the material is tendered by oxycellulose formation; (2) the yellow or orange dyestuff is wholly or partly bleached; (3) the shade is altered; (4) a second dye (e.g. Ciba Blue 2B) present in admixture is wholly or partly bleached.[81] Similar effects are obtained by replacing hydrogen peroxide by hypochlorite.[83]

When cotton dyed with certain red, orange and yellow vat dyes is "chemicked" (treated with hypochlorite solution) in daylight, excessive tendering may occur. Lanigan[84] has developed a technique for observing this phenomenon which yields spectacular results. When calico or viscose sheet impregnated with solutions of hypochlorite or hydrogen peroxide, or merely exposed to moist air, is irradiated with the full mercury spectrum, and the irradiated samples are developed in a hot alkaline complex silver solution, metallic silver is deposited in location and amount determined by the formation of oxycellulose with reducing properties as a result of the photochemical oxidation of cellulose. With undyed cellulose, a "degradation spectrogram" is thus obtained in which the lines in the ultraviolet region of the mercury spectrum are developed; but using cellulose dyed with the active vat dyes, the "degradation spectrogram" shows the lines in the visible region of the spectrum. Maximum tendering is in the pH range 7.0–7.5, and there is also considerable tendering below pH 7.00. Comparatively little degradation takes place at pH 10–11, and this alkalinity must be maintained in bleaching colored fabrics containing the active dyes. The very active dyes, such as Cibanone Yellow R, cannot be used at all with safety in materials which have to be subsequently bleached. Cotton dyed an azoic yellow by means of Naphtol AS–G and Red Salt AL (diazonium salt of α-aminoanthraquinone) accelerates the oxidizing action of hypochlorite; the anthraquinone component is apparently responsible for the tendering action, since other azoic yellows (e.g., Naphtol AS–G in combination with diazotized dichloroaniline) are quite inactive.

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[81] *J. Soc. Dyers Colourists* **45,** 175 (1929).

[82] Brear, *Textile J. Australia* **15,** 132 (1940).

[83] See also Derrett-Smith and Nodder, *J. Textile Inst.* **23,** T293 (1932).

[84] *J. Textile Inst.* **39,** T285 (1948).

While photochemical oxidation by air and by hypochlorite may be assumed to be closely related, the quantitative behavior of individual vat dyes in the two oxidation processes is different, probably because the comparison is made under arbitrarily chosen sets of conditions.[85] The very active dyes, such as Cibanone Yellow R, Anthra Yellow GC, Indanthrene Golden Orange G, Pyranthrone and Indanthrene Yellow FFRK, are active in both air and hypochlorite oxidations. Grelanone Red 2B (Indanthrene Rubine R), Caledon Red 2G (Indanthrene Red GG) and Caledon Yellow G (Flavanthrone) are practically inactive in photochemical air oxidation, but are very active in the photochemical hypochlorite oxidation.

An observation of interest in connection with these accelerated oxidations of cellulose is the catalytic effect of hydrogen peroxide on the reaction between an easily oxidizable dye (e.g. Orange II) and sodium hypochlorite; the destruction of the dye by means of hypochlorite, which under specified conditions takes 15 minutes, is complete in a few seconds when a trace of hydrogen peroxide is added.[86]

The photodegradation of vat-dyed viscose is suppressed, partly or completely according to the nature of the dye exposed, by drying acidified formaldehyde into the yarn and heating at 100°; or by applying a thiourea-formaldehyde precondensate as for an anticrease treatment (impregnating, drying and curing at 130° in presence of an acid catalyst);[87] or by aftertreatment with a reaction product of formaldehyde and dicyandiamide or melamine.[88] During such formaldehyde treatments, cross linkages between hydroxyl groups in neighboring cellulose chains are probably formed by the intervention of methylene groups or more complex groups resulting from the condensation of formaldehyde with urea and similar reagents.[89] The number of hydroxyl groups available for oxidation is thus reduced. According to a patent claim, the resistance of vat-dyed cellulose fibers to the action of light is increased by treatment with a solution of lower oxidation salts of manganese, cobalt, lead or copper;[90] Egerton has shown that copper hydroxide and aluminum hydroxide reduce the photochemical degradation of cellulose in air at 100% R.H., but not in dry air and not in presence of the active vat dyes.[80] Copper and other metals, which in minute amounts exert a large effect on the photochemical action of all classes of dyes, prevent the liberation of hydrogen peroxide by irradiation of dyed cotton in moist air.[80] Indanthrene Olive Green B improves the light fastness of Indanthrene Yellow GF and suppresses the lowering of fiber strength by the yellow dye; other blue and green dyes have some protective action, but none is so effective as Olive Green B.[91]

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[85] Clibbens and Little, *J. Textile Inst.* **37,** T219 (1946).

[86] Kauffmann, *Ber.* **65,** 179 (1932).

Mechanism of the light-tendering activity of dyes. The photochemical degradation of cellulose in presence of the active vat dyes is essentially a photosensitized process in the sense that energy is transferred from the spot at which light is absorbed to another at which a chemical reaction takes place. Many reactions are known to be photosensitized by dyes.[49] It has been suggested that the mechanism of the activity of the anthraquinonoid vat dyes involves the preliminary reduction of a quinone to the leuco compound, the reoxidation of the leuco compound to the parent vat dye by air and the simultaneous formation of hydrogen peroxide together possibly with a dyestuff peroxide.[92] The reduction of the anthraquinone nucleus to the anthrahydroquinone may be assumed to be accompanied by an equivalent dehydrogenation of cellulose, so that some oxycellulose formation may take place at this stage. Although there are examples of dye-sensitized photochemical reductions (e.g., the chlorophyll-sensitized reduction of Methyl Red by phenylhydrazine),[93] there has been no real evidence so far that the active vat dyes undergo a photoreduction to the leuco derivatives. Certain color changes observed when an active dye (e.g., Cibanone Orange R and Yellow R, Hydron Yellow GG, and Anthra Yellow GC) on cotton is illuminated have been cited by Scholefield and Goodyear as indicating the formation of leuco compounds;[94] but the colors of the leuco acids of Cibanone Yellow R, Hydron Yellow GG and Anthra Yellow GC are yellow or reddish yellow, and these minor color changes cannot be relied upon as proof of photoreduction.

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[87] Boulton, XI International Congress of Pure and Applied Chemistry, 1947.

[88] Ciba, BP 582,143; USP 2,435,591.

[89] Cf. Meunier and Guyot, *Rev. gén. colloïdes* **7,** 53 (1929); Cameron and Morton, *J. Soc. Dyers Colourists* **64,** 329 (1948).

[90] IG, DRP 736,882.

[91] Müller, *Melliand Textilber.* **28,** 389 (1947).

[92] Scholefield and Turner, *J. Textile Inst.* **24,** P130 (1933).

The cellulose substrate can be replaced by other oxidizable substances; when a suspension of an active vat dye in alcohol is illuminated, acetaldehyde is formed.[95] Bamford and Dewar have shown that the active vat dyes initiate the autoxidation of tetralin and the polymerization of styrene.[96, 4a] No correlation of cellulose tendering with styrene polymerization was noticed, and in Table V the dyes are arranged in order of activity in cellulose-tendering, which corresponds very roughly to the quantum yields in the tetralin oxidation. The figures in column 2 of Table V represent the increase in fluidity (determined in a modified cuprammonium solution containing 1% of cuprous chloride) when dyed viscose was exposed under glass to daylight (with some sunlight) for two months. The tetralin oxidation apparently involves a direct dehydrogenation by the excited dye; Bamford and Dewar suggest that in the absence of moisture there is a similar direct attack of the cellulose substrate. In their view the primary step in the photochemical activity of a vat dye in the presence of oxygen and water is the oxidation of hydroxyl ion to hydroxyl radical by the excited dye molecule, and the low quantum yield is probably due to the reversibility of this process. In earlier work by Weiss photosensitized reactions in solution have been represented by mechanisms involving free radicals and radical ions, the initial step being interaction between an electronically excited form of the light-absorbing molecule and a suitable acceptor molecule.[50, 4a] The part that is probably played by semiquinone ions in the photochemical activity of anthraquinone derivatives is discussed later.

The formation of hydrogen peroxide in titratable quantities, when an

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[93] Ghosh and Sen Gupta, *J. Ind. Chem. Soc.* **11,** 69 (1934); see also *Livingston et al., J. Phys. &. Colloid Chem.* **51,** 775 (1947); *JACS* **70,** 1510 (1948).

[94] In Ref. 72, the reference of the authors to the coupling of the leuco compounds with diazonium salts is totally inexplicable.

[95] Sadasivan, quoted by Scholefield and Turner; see also Meyer and Eckert, *Monatsh.* **39,** 249 (1918). Eckert, *Ber.* **58,** 313 (1925), has shown that numerous substances are oxidizable in the presence of anthraquinone, light and air.

[96] Bamford and Dewar, *Nature* **163,** 214 (1949).

TABLE V
(Bamford and Dewar)

Dye	*Increase in fluidity* ΔF *(poise^{-1})*	*Quantum yield* $\eta \times 10^2$
Caledon Dark Brown 2G	1.5	0.004
Cibanone Black 2B	1.7	0.00004
Cibanone Blue RSN	1.8	∼0
Caledon Pink RL	2.0	0.002
Cibanone Brilliant Green BF	2.1	0.00001
Caledon Blue RN	2.2	∼0
Undyed cellulose	2.3	—
Cibanone Navy Blue RA	2.4	0.0004
Paradone Yellow G (new)	2.5	0.04
Paradone Yellow 3RT	2.6	—
Caledon Jade Green XN	2.6	0.0002
Caledon Blue GCP	2.9	∼0
Paradone Brilliant Orange RK	2.9	0.3
Caledon Dark Blue MBA	3.1	0.001
Cibanone Brown BG	3.2	0.0007
Caledon Jade Green 2G	3.3	0.0004
Cibanone Brown GR	3.3	0.0002
Flavanthrone (pure)	3.4	0.3
Cibanone Violet 4R	3.7	∼0
Cibanone Yellow 3R	3.7	0.06
Paradone Brilliant Orange GR	3.9	∼0
Caledon Brilliant Orange 6R	4.0	1
Indanthrene Yellow 3RT	4.1	0.3
Cibanone Olive 2R	4.3	∼0
Cibanone Yellow G	4.3	0.08
Caledon Orange RRT	4.5	0.03
Caledon Yellow GN	4.6	0.3
Caledon Yellow 4G	4.7	—
Cibanone Orange 8R	4.7	0.02
Caledon Red BN	4.7	0.2
Cibanone Yellow GN	4.7	0.08
Cibanone Yellow 3RF	5.1	—
Ciba Blue 2B	5.1	∼0
Cibanone Orange 2RT	5.4	0.003
Caledon Gold Orange 3G	5.5	—
Cibanone Brilliant Orange RK	5.6	0.05
Cibanone Red FBB	5.7	0.1
Cibanone Red 4B	5.8	0.007
Cibanone Brilliant Orange GK	5.9	0.3
Cibanone Orange 2R	6.1	0.3
Cibanone Golden Orange 2R	6.3	0.2
Cibanone Golden Orange 3G	6.4	0.0004

TABLE V (*Continued*)

Dye	*Increase in fluidity* ΔF *(poise*$^{-1}$*)*	*Quantum yield* $\eta \times 10^2$
Cibanone Red BN	6.5	0.002
Caledon Gold Orange G	6.6	0.02
Cibanone Orange 3R	6.8	0.2
Cibanone Brilliant Green 4G	6.9	~0
Cibanone Red G	7.1	—
Anthanthrone	7.2	1
Cibanone Golden Yellow RK	7.3	0.9
Cibanone Yellow GK	7.4	0.06
Cibanone Golden Orange GN	7.7	0.1
Cibanone Red 2B	8.1	0.01
Cibanone Golden Orange G	8.1	—
Cibanone Orange 6R	8.2	0.3
Paradone Yellow 5GK	8.6	0.2
Paradone Golden Yellow GK	8.6	0.7
Cibanone Yellow 5GK	9.4	0.004
Cibanone Orange R	9.7	4.0
Indanthrene Yellow FFRK	10.4	0.07
Pyranthrone (pure)	10.8	0.02
	(Mercury arc exposure)	
Paradone Yellow GCX	11.6	3
Paradone Yellow GC	13.6	8
Cibanone Golden Yellow GK	13.8	0.1
Caledon Yellow 5G	13.9	10
Caledon Golden Yellow GK	14.3	0.5
Cibanone Yellow 3G	14.7	0.03
Cibanone Yellow 2GR	14.8, 17.7	5
Ciba Yellow G	18.9	0.01
Cibanone Yellow R	26	0.7

anthraquinone suspension in water or a dyeing of an active vat dye is submitted to the action of light in the presence of moisture and oxygen, has been conclusively determined.[72, 74] When samples of an undyed fabric and a fabric dyed with an active vat dye are exposed at a distance from each other, increased tendering of the undyed material has been observed at distances of up to 8 mm.; a volatile agent, which may be hydrogen peroxide or activated oxygen, must be responsible for the effect.[78, 97, 98]

Reactions in which the oxidation of a readily oxidizable substance by air or other oxidizing agent brings about a simultaneous oxidation of a

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[97] Hill, *Chemistry & Industry* **45,** 691 (1947).

[98] Egerton, *Textile Res. J.* **18,** 659 (1948).

second substance are well known.[99] The formation of hydrogen peroxide when leuco indigo undergoes oxidation in air, especially in presence of alkali, was noticed by Schönbein in 1860.[100] Manchot's observation,[101] also made many years ago, that hydrogen peroxide is formed when anthrahydroquinone absorbs oxygen has led to a technical process for the production of hydrogen peroxide using 2-ethylanthraquinone.[102] Azobenzene, *p*-dimethylaminoazobenzene and amino-substituted hydrazo compounds have also been suggested for the same purpose.[103] In the reaction between ferrous salts and hydrogen peroxide, free hydroxyl radicals ($HO^\bullet$) are produced and they are capable of oxidizing organic compounds of many types.[104] These are examples of autoxidation in which photosensitization is not involved. Using a technique in which the dyes are adsorbed on separate particles of silica gel, it has been shown that oxygen becomes activated to a metastable condition and passes to leuco Malachite Green, when the oxidation is photosensitized by Trypaflavine.[105] The bleaching of fluorescein dyes by light is probably a process of oxidation by hydrogen peroxide, the formation of the latter requiring an activation of the dye molecule by light.[106] IG research has established that the fading of dyes on cellulose acetate delustered by titanium oxide is due to peroxide formation.[107] Zinc oxide, which is a powerful accelerator for the photochemical oxidation of cellulose, produces hydrogen peroxide when it is irradiated in presence of water and air.[108]

The action of hypochlorite on cellulose in presence of reduced vat dyes. The accelerated photochemical oxidation of cellulose in presence of reduced vat dyes is paralleled by the action of chemical oxidizing agents such as hypochlorite.[109] In the presence of the leuco derivatives of certain vat dyes, the oxidation of cellulose is greatly accelerated; similar effects of other reducing agents (e.g. oxalic acid)[110] in accelerating the action of oxidizing agents on cellulose have also been noticed. Scholefield, Nabar and their collaborators have made extensive studies of the phenomenon, and have observed interesting relationships between various factors. The extent of the accelerated oxidation is related to the potential of the oxidizing agent.[109] The increase in copper number and carboxyl content by the accelerated oxidation of cellulose is directly proportional to the oxygen consumption. Hypochlorite oxidation at pH 7.55 increases with increase in concentration of the active dye, and at each concentration the ratio between the copper number and the number of carboxyl groups is a constant, which is independent of the pH of the hypochlorite and the concentration of the accelerator. Hypochlorite oxidation of cotton dyed with Caledon Yellow G and Indanthrene Yellow FFRK, which are not altered by the hypochlorite, results in a constant ratio of 1.25 between copper number and carboxyl groups. When Indanthrene Blue R or Ciba Blue 2B, which are altered by the hypochlorite, are used, this ratio is halved, indicating that a different oxidation reaction occurs.[111]

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[99] Gebhardt, *J. Soc. Dyers Colourists* **29,** 249 (1913); see also *Annual Repts. Chem. Soc. London* **22,** 117 (1925).

[100] *J. prakt. Chem.* **81,** 16 (1860).

[101] Manchot and Herzog, *Ann.* **394,** 129 (1901); *ibid.* **396,** 318 (1901).

[102] IG, BP 465,070; *CIOS* Item No. 22, File No. XIX-4.

[103] Mathieson Alkali Works, BP 461,589.

[104] Haber and Weiss, *Proc. Roy. Soc. London* **147A,** 332 (1934); Merz and Waters, *JCS* S15 (**1949**).

[105] Kautsky *et al., Ber.* **66,** 1588 (1933); see also *ibid.* **64,** 2053, 2677 (1931); **65,** 401 (1932); *Trans. Faraday Soc.* **35,** 216 (1939).

[106] Blum and Spealmann, *J. Phys. Chem.* **37,** 1123 (1933); Chakravarti and Dhar, *Z. anorg. allgem. Chem.* **142,** 299 (1925); see also Gaffron, *Ber.* **60,** 755, 2229 (1927).

[107] *BIOS* **987.**

[108] Baur and Neuweiler, *Helv. Chim. Acta* **10,** 901 (1927); Chari and Qureshi, *J. Indian Chem. Soc.* **21,** 97 (1944).

[109] Nabar, Scholefield, and Turner, *J. Soc. Dyers Colourists* **51,** 5 (1935); **53,** 5 (1937); Mehta and Turner, *ibid.* **63,** 15 (1947).

It is necessary to emphasize that these relationships do not hold for unaccelerated oxidations of cellulose which are much more complicated and variable in the nature and degree of the modifications. The difference between the oxidation potential of the oxidizing agent and the reduction potential of the vat dye may be the determining factor in the acceleration of the oxidation.[109] Joshi and Nabar[111] have measured reduction potentials of Cibanone Orange R at various pH values, and have found that the curve relating pH to oxygen uptake[109] closely resembles the curve showing the relation between the pH and the difference between the oxidation potentials of hypochlorite solutions and the reduction potentials of Cibanone Orange R. A few other dyes examined show similar behavior.

An important fact to be borne in mind is that the oxidation of cellulose, when a leuco vat dye on the fiber is treated with an oxidizing agent, is distinct from the photochemical oxidation and is to some extent independent of the color of the dye. Thus, when a reduced dyeing at pH 7 is submitted to air oxidation in the dark, Ciba Blue 2B produces more degradation of the cellulose than Indanthrene Yellow FFRK.[112] Examining a series of 55 vat dyes (anthraquinonoid as well as thioindigoid) for their effect on the rate of oxidation of cellulose by hypochlorite solutions at various pH values and in the presence and absence of light, Clibbens and Little[85] found no relationship between chemical constitution and activity in promoting oxidation. The critical factor is the pH of the hypochlorite or other oxidising agent, and at the optimum pH blue and green vat dyes can promote the tendering of cellulose when the reduced dyeings are submitted to oxidation in the dark. The acceleration of the oxidizing action of the hypochlorite is pronounced only under acid conditions, which are not likely to arise in normal technical processes.[85] Even air oxidations of reduced dyeings of photochemically inactive dyes can result in tendering of the cellulose.[112] If a vat dye on cotton is repeatedly reduced and reoxidized, there is an increase in fluidity with each cycle for nearly every vat dye, but the greatest rise in fluidity results from the light-tendering dyes and the increase in fluidity with nontendering dyes (e.g., Ciba Blue 2B, Caledon Blue R, Caledon Jade Green X) is small.[112] When the leuco compound of anthraquinone or an anthraquinone vat dye is reoxidized by air or sodium hypochlorite one mole of hydrogen peroxide is formed for each reduced quinone group undergoing oxidation, but this quantitative relationship is independent of the light-tendering activity of the dye.[113] Ferrous hydroxide, deposited on the fiber, causes a marked acceleration of the oxidation of cellulose by hypochlorite, the magnitude of the acceleration being of the same order as that produced by leuco derivatives of the most active vat dyes.[114] While the work of Nabar, Scholefield and Turner has thrown much light on a complex and exceedingly important problem, there are many aspects of the behavior of vat dyes and their leuco compounds as oxygen carriers in cellulose oxidations which are yet unsolved.

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[110] Clibbens and Ridge, *J. Textile Inst.* **18,** T135 (1927).

[111] Joshi and Nabar, *Nature* **159,** 711 (1947); Mhatre, Nabar, and Vyas, *Proc. Indian Acad. Sci.* **31A,** 234 (1950).

[112] Brear and Turner, *J. Soc. Dyers Colourists* **61,** 273 (1945).

Chemical Constitution of the Active Vat Dyes

Anthraquinone and its simple derivatives have a small but definite effect on the photochemical oxidation of cellulose; methyl and halogen substituents, particularly in the 2-position, increase the activity.[92] A factor which accentuates the effect with the anthraquinonoid vat dyes is the affinity of the leuco compounds for cellulose and the intimacy of the cellulose-dye union, enabling the carrier action of the dye to be exercised more effectively. Whatever may be the mechanism of the action of light on a cellulose-dye system, the orientation and packing of the dye molecules in the fiber must therefore affect the process. It follows that the factors influencing the affinity of a dye for cellulose, such as the shape

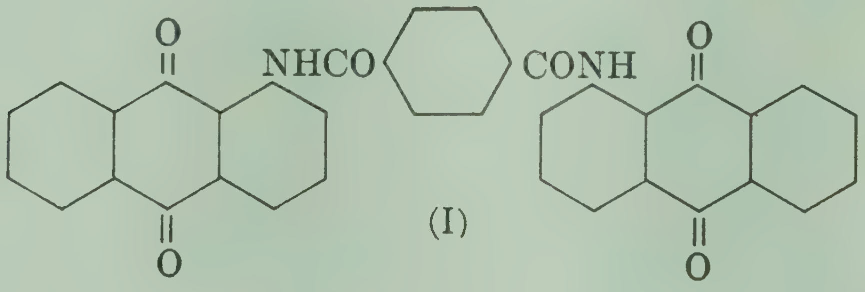
[113] Atherton and Turner, *J. Soc. Dyers Colourists* **62,** 108 (1946).

[114] Nabar and Turner, *J. Soc. Dyers Colourists* **61,** 258 (1945); see also Turner, *ibid.* **61,** 255 (1945).

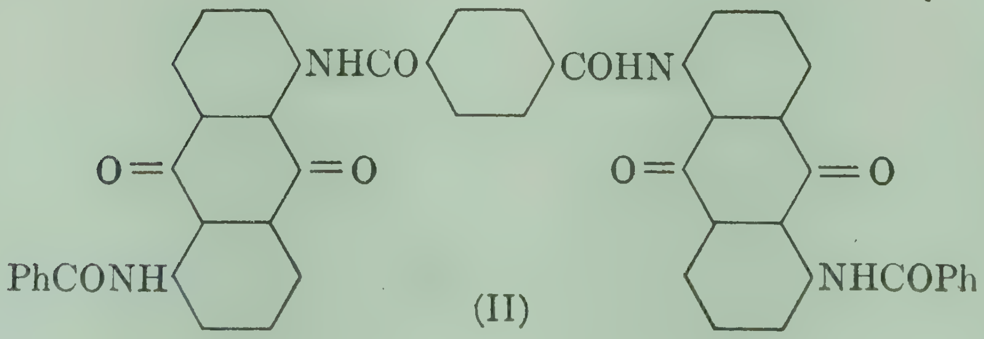
and size of the dye molecules, and the nature, number and distribution of groups capable of hydrogen-bond formation with the hydroxyl groups of cellulose, must be involved in the photochemical action. Such factors account in part for the differences noticed by Landolt (Table III)[4a] in the photochemical activity of 1,5-bis-aroylamidoanthraquinones (e.g., the *o*- and *p*-chlorobenzoyl derivatives).

Pronounced light-tendering activity is found in certain chemical types among the anthraquinone vat dyes, such as the benzamidoanthraquinones, anthrimides and carbazoles; but all the dyes of each class are not active. It is mainly the yellows and oranges which are active, so far as the acceleration of the photochemical oxidation of cellulose, as distinct from the purely chemical oxidations, is concerned. Further, the yellow dyes of a given chemical type are more active than the orange dyes, and in general, a bathochromic shift in the absorption spectrum in the visible region results in a reduction of the light-tendering activity.

Most of the yellow and orange benzamidoanthraquinones are active, and examples are Algol Yellow WG (1-benzamidoanthraquinone), Indanthrene Yellow GK (1,5-bisbenzamidoanthraquinone), Paradone Yellow 5GK (I), and Indanthrene Yellow 5GK which is the isomer of (I) from isophthalic acid. *β*-Aminoanthraquinone derivatives appear to be more active than the *α*-isomers; bis-*β*-anthraquinonylurea (Algol Yellow 4GK; Helindone Yellow 3GN), no longer used as a dye, was the most powerful tenderer among the series of dyes examined by Landolt. A notable exception is Caledon Yellow 4G (II), which is inactive;[70] but its light fastness (4–5) is not sufficiently high for use on casement fabrics. Since (II) is derived from (I) by the introduction of two benzamido groups and both are yellow dyes, we have a clear demonstration of the fact that the benzamido group *per se* is not responsible for the activity of



(I)



(II)

the benzamidoanthraquinones. At first sight, the inactivity of (II) may be ascribed to the chelation of all the carbonyl groups with neighboring NH groups by hydrogen bonding; but this would also be true of Caledon Yellow 3G (1,5-bisbenzamidoanthraquinone), which is classified among the active dyes. When the terephthaloyl group in Caledon Yellow 4G is replaced by an oxalyl group, as in Indanthrene Yellow 3GF, tendering activity to a moderate extent is restored; Fox[71a] classifies Indanthrene Yellow 3GF among inactive dyes. Conflicting statements have been made regarding the behavior of the orange and red benzamidoanthraquinones. According to Egerton (Table I), 1,4-bisbenzamidoanthraquinone (Indanthrene Red 5GK) and 1,4,5-trisbenzamidoanthraquinone (Caledon Red X5B) have little or no activity, while 1,2,4-trisbenzamidoanthraquinone (Indanthrene Orange RRK) is definitely active, being somewhat more potent as a tenderer than 1-benzamidoanthraquinone. Landolt classifies both Indanthrene Red 5GK and Indanthrene Orange RRK among the active dyes, but the former is stated to be much more active. Fox has stated that Indanthrene Orange GG (the condensation product of isophthalic acid with one mole each of 1-amino-4-benzamidoanthraquinone and 1-amino-5-benzamidoanthraquinone) is not merely inactive, but exercises a protective action on cellulose.[71a] The introduction of a hydroxyl group in the anthraquinone nucleus deepens the color and diminishes the photochemical activity. An example is 1,5-bisbenzamido-8-hydroxyanthraquinone (Algol Red R and FF) which is considerably less active than Indanthrene Yellow GK; when a second hydroxyl group is introduced, the dye (Indanthrene Violet BBK) has very little activity.

1,2′-Dianthrimide (Indanthrene Orange 6RTK) is as active as pyranthrone according to Landolt, and inactive according to Egerton. Indanthrene Yellow FFRK, the carbazole prepared by the cyclization of 1,1′-dianthrimide, is a powerful tenderer; but when two benzamido groups are introduced in the 5,5′-positions, the dye (Indanthrene Golden Orange 3G) is practically inactive; when the benzamido groups are in the 4,5′-positions the dye (Indanthrene Brown R or FFR) is a nontenderer and has protective action.[71a] Landolt[4a] records considerable activity for Indanthrene Golden Orange 3G by the "blue test." The influence of color on tendering activity is shown by the two isomeric dicarbazoles, Indanthrene Yellow 3RT and Indanthrene Brown BR; the former is as active as Algol Yellow WG while the brown dye is not merely nontendering, but appears to have a slight protective action on cellulose exposed to light. Cotton dyed with another carbazole derivative, Indanthrene Khaki GG, is likewise less degraded by the action of light than undyed cotton.

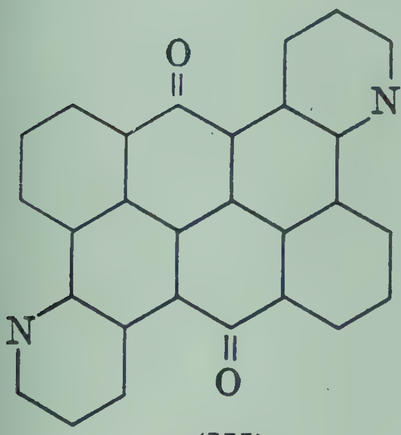
There are no tenderers among the acridones; dyes such as Indanthrene Orange F3R, Indanthrene Red BN (or RK), Indanthrene Brilliant Pink BBL and Indanthrene Turquoise Blue are completely innocuous; but before concluding that the acridone ring system as such renders an anthraquinone vat dye inactive, more orange dyes will have to be examined, and it must also be remembered that there are no yellow dyes containing the anthraquinone-acridone ring system. According to Fox, Indanthrene Orange RR (the condensation product of anthraquinone-acridone-10-carboxylic acid and 1-amino-5-benzamidoanthraquinone) is highly protective.

Pyranthrone (Indanthrene Golden Orange G) and its dibromo and tribromo derivatives (Indanthrene and Caledon Orange 2RT, Indanthrene and Caledon Orange 4R) have marked light-tendering activity, but the bromo compounds are less active. Landolt classifies dichloroanthanthrone (Indanthrene Brilliant Orange GK) as a safe dye; Egerton finds that it is somewhat more active than Algol Yellow WG, but that the dibromo compound (Indanthrene Brilliant Orange RK) is less active and comparable to Indanthrene Golden Orange 3G. In his more recent work (Table III) Landolt records the activities in terms of the blue test percentages as 1.5, 7, and 6.5 for anthanthrone and its dichloro and dibromo derivatives. Indanthrene Golden Yellow GK and RK which are dibenzopyrenequinones are active dyes; as in other types, the dichloro compound (GK) is more active than the dibromo compound (RK) and is among the most powerful tenderers; the parent dibenzopyrenequinone is more active than its halogen derivatives.

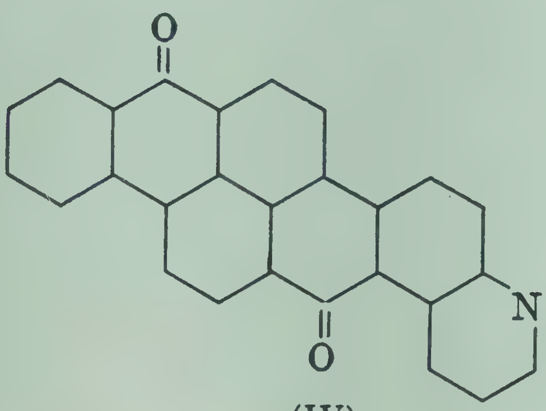
The sulfurized anthraquinonoid vat dyes, Cibanone Yellow R and Orange R, Indanthrene Yellow GF and Anthra Yellow GC, are extremely active dyes; and Cibanone Yellow R, which is probably the most active tenderer known, is usually the dye of choice for investigating the influence of various factors on the photochemical oxidation of cellulose in presence of dyes. Indanthrene Yellow GF and Anthra Yellow GC are thiazole derivatives. The essential constituent of Cibanone Yellow R is derived from β-methylanthraquinone and probably has a structure in which there is no sulfur-containing ring system. Another powerful tenderer, obsolete as a dye, is Anthraflavone (sym. bis-β-anthraquinonylethylene), which has poor fastness to light; but the green shades produced by a mixture of Anthraflavone and Indanthrene Blue have good light fastness and they do not accelerate the photochemical degradation of cellulose.

The imides of perylenetetracarboxylic acid (e.g., Indanthrene Red GG and Indanthrene Scarlet R) and the imidazoles derived from naphthalenetetracarboxylic acid (Indanthrene Scarlet GG and Indanthrene Brilliant Orange GR) are inactive.

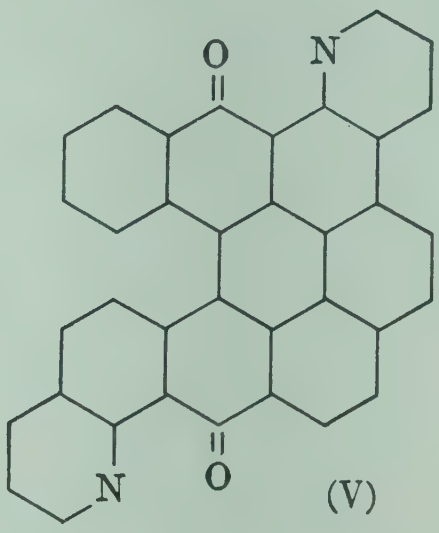
Flavanthrone (Indanthrene Yellow G) has long been known to be a safe dye from the point of view of light-tendering; but unfortunately, as so frequently happens because of the different structural requirements for various fastness properties, it has poor fastness to alkali. Yellow vat dyes which have no light-tendering activity and are otherwise satisfactory have therefore been sought for. As the result of a study of the structural features of the known tendering dyes, Kunz concluded that the tendering activity is related to the chemical constitution of the dye, especially the 1,4-quinone group; he then instituted a systematic search for different types which are inactive, and made the important discovery that vat dyes possessing basic character because of the presence of pyridine or pyrimidine rings are nontendering.[115] Thus anthanthrone, 2,3,7,8-dibenzopyrene-1,6-quinone, *allo-ms*-naphthodianthrone and pyranthrone, which are all powerful tenderers, become completely innocuous by the fusion of one or more pyridine rings; examples are (III), (IV), (V), and (VI). Other effects of the introduction of pyridine and pyrimidine rings are increased solubility, affinity and levelling power, and decreased stability to alkaline treatments. Vat dyes from ceramidonine (VII) are inactive, but have no practical value because of their low fastness to light, showing that fastness to light and nontendering character



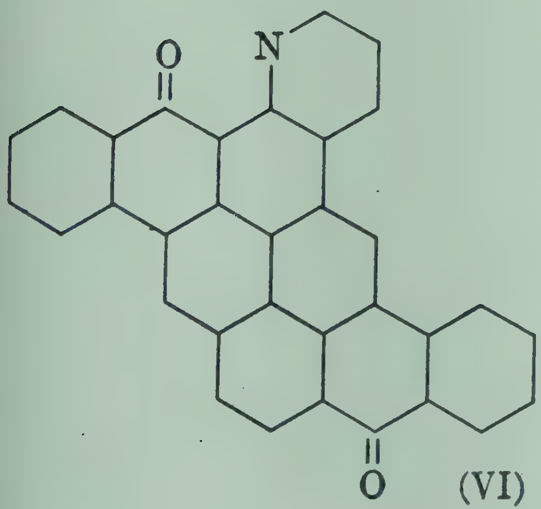
(III)



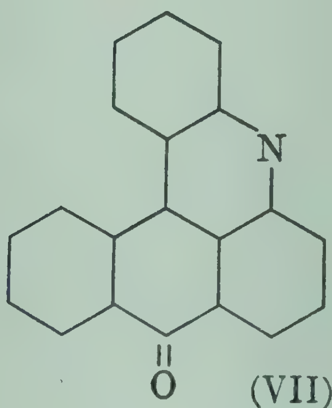
(IV)



(V)



(VI)



(VII)

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[115] *Z. angew. Chem.* **52**, 269 (1939).

do not necessarily go together. Kunz has found, however, that the superior light fastness of flavanthrone (or diazapyranthrone) in comparison with its carbocyclic analog, pyranthrone, is to be ascribed to the nitrogen atoms in the ring system, and that this is true in general of dyes derived from the azabenzanthrones, pyridinodibenzopyrenequinones, and other groups of dyes which have better light fastness than similar, completely carbocyclic compounds. If the NH groups in indanthrone or in the anthraquinoneacridones are replaced by sulfur or oxygen, the fastness to light is adversely affected. The pyridine, pyrimidine or other nitrogen-containing ring need not be part of the fused ring system to produce nontendering dyes; a nitrogen heterocycle introduced as an external group is adequate, and acylamidoanthraquinones in which the acid half is derived from pyridine, quinoline, acridine and acridone are nontendering. On the other hand, yellow and orange dyes containing the triazine ring, which are prepared by the condensation of aminoanthraquinones with cyanuric chloride, are active as catalysts for the action of light on cellulose.[116] Cibanone Orange 6R (cyanurated 1-amino-4-methoxyanthraquinone) is more active than Algol Yellow WG. There are also other examples in conflict with the Kunz hypothesis, such as Algol Yellow GC and Indanthrene Yellow GF, which are thiazole derivatives and are tenderers.

Following the investigations of Kunz, IG have made two valuable additions to their vat dye range; Indanthrene Yellow 4GK and 7GK are pyrimidanthrones which have very good fastness to light (6–7) and are free from the tendering defect. Strong absorption in the region 3600–4000A has been considered to be concerned in the photochemical activity of yellow and orange vat dyes, and it has been shown that the safe dye Indanthrene Brilliant Orange GR has negligible absorption at 3600–4000A.[92] However, 1-benzamidoanthraquinone (Algol Yellow WG), an active dye, as well as Indanthrene Yellow 4GK and Indanthrene Yellow 7GK have similar absorption curves (Fig. 1); the pyrimidanthrones have considerably higher intensity of absorption in the region 4200–4500A.[117]

From a study of the available data and the relevant theoretical considerations, the activity of a dye in accelerating the photochemical oxidation of cellulose would appear to depend on a combination of several factors of which the color is only one. Shaffer[118] has drawn attention to the rapidity of oxidations and reductions involving one-electron changes, in contrast to the slow ionic reactions involving simultaneous two-electron changes such as ($Tl^+ \rightarrow Tl^{+++}$) or ($I_2 \rightarrow 2I^-$). He regards the catalytic activity of quinones as being due to their ability to accept electrons singly, and he has indicated the relation of this property of reversible organic oxidation-reduction systems to the reduction of oxygen to hydrogen peroxide in biological oxidations. Semiquinone formation is probably also significant in the photochemical degradation of cellulose in presence of anthraquinone derivatives, moisture and alkali having a marked effect on the action. Michaelis and Smythe have postulated as a general principle that "the inertia of organic compounds towards oxidizing agents is due to the fact that the oxidation can proceed at a measurable speed only in two successive univalent steps and consequently only if the intermediate free radical can be formed."[119] Thus oxidations are rapid if there is resonance-stabilization of the semiquinone radicals. Appleton and Geake have obtained from the redox titrations of vat dye systems evidence of the formation of the intermediate semiquinones in several instances.[120] Visual evidence was especially striking in the case of Indanthrene Golden Yellow GK (2,3,7,8-dibenzopyrene-1,6-quinone), which gives a clear red vat of the dihydro compound and a blue semiquinone. It is suggested that the redox potential of the quinone, which is known to be a measure of its oxidizing power, and the stability of the anionic semiquinone are both concerned in the acceleration of the photochemical oxidation of cellulose by certain anthraquinonoid vat dyes,

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[116] Blinov, *Tekstil. Prom.* **5,** No. 11–12, 47 (1945).

[117] Sunthankar and Venkataraman, *Proc. Indian Acad. Sci.* **32A,** 240 (1950).

[118] *J. Phys. Chem.* **40,** 1021 (1936).

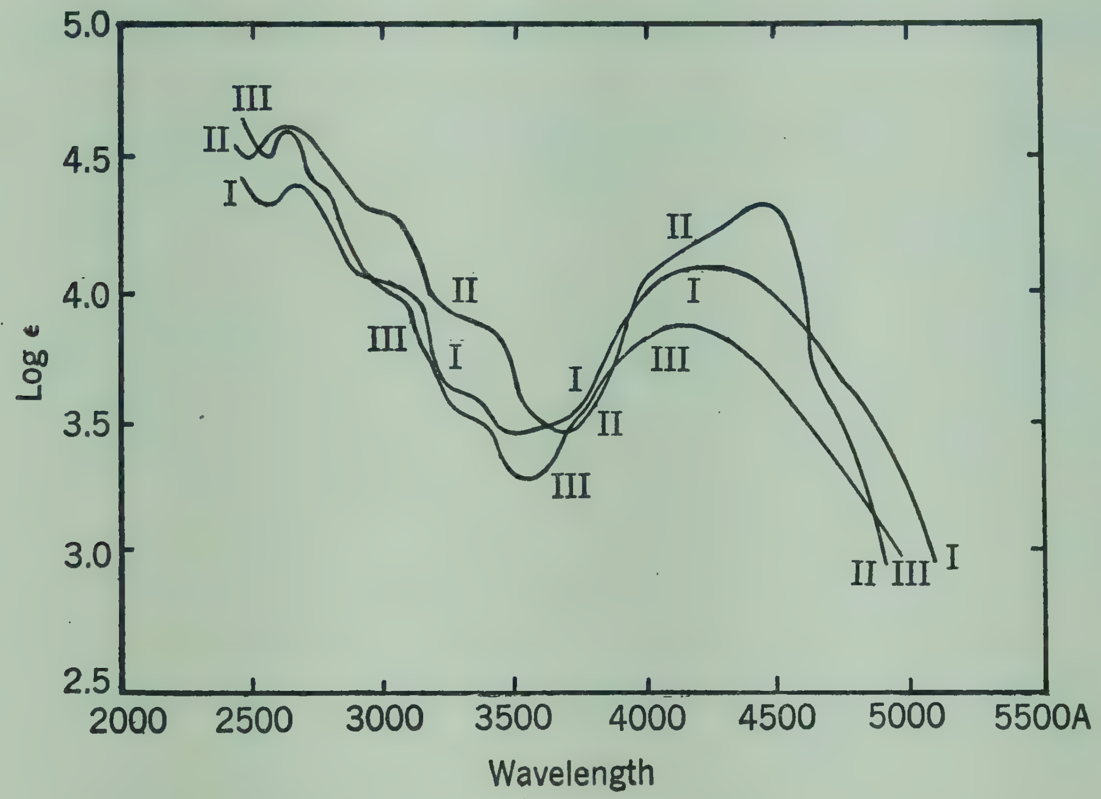

Fig. 1. Absorption spectra of (I) Indanthrene Yellow 4GK; (II) Indanthrene Yellow 7GK; and (III) α-Benzamidoanthraquinone (in cellosolve).

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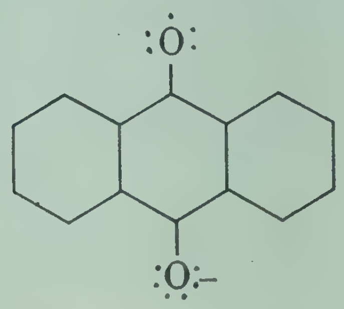
[119] *Ann. Rev. Biochem.* **7,** 6 (1938).

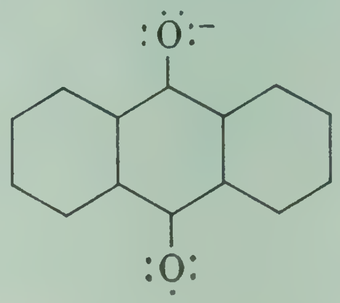
[120] *Trans. Faraday Soc.* **37,** 45 (1941); see Chapter XXX for further references to semiquinone formation in the anthraquinone vat dyes.

together with their light absorption characteristics which determine the quanta of energy available.[117]

The semiquinone anion from anthraquinone is stable because of the equivalence of the two structures (A) and (B). Yellow dyes such as



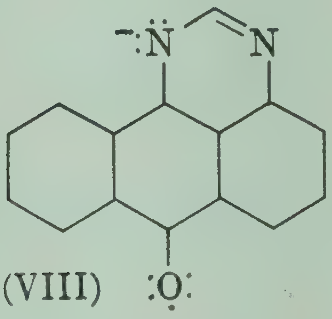
(A)



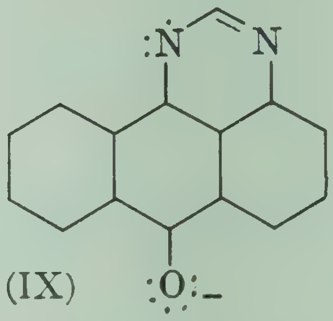
(B)

Indanthrene Yellow FFRK and Anthraflavone are very active, and four equivalent structures can be written for the semiquinone ion of the dihydro compound.

The stability of the semiquinone ion of a pyrimidanthrone must be relatively small, since the structures (VIII) and (IX) are not equivalent, and the pyrimidanthrone derivatives, Indanthrene Yellow 4GK and

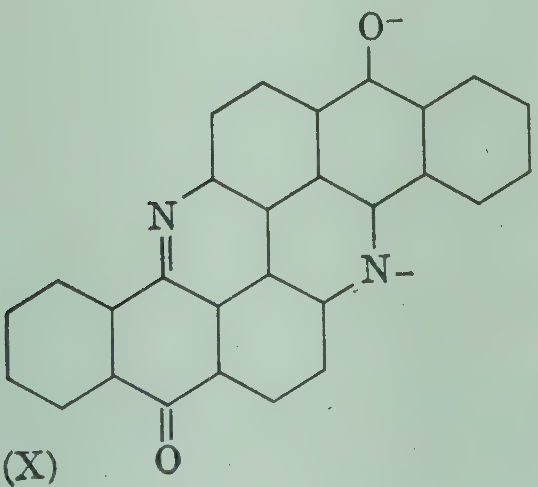


(VIII)

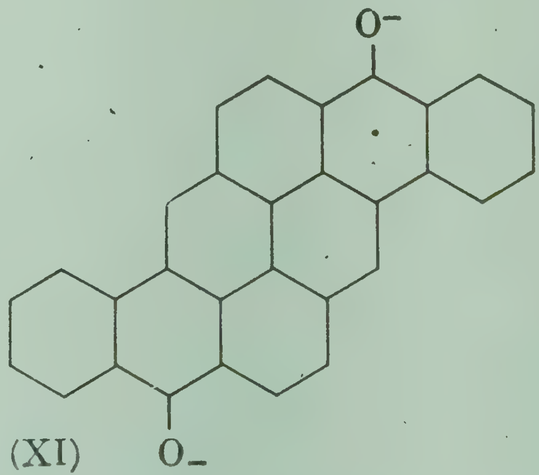


(IX)

7GK, are therefore comparatively inert in catalyzing the photochemical oxidation of cellulose. The difference between flavanthrone and pyranthrone, the latter being much more active as a tenderer, may be attributed to a similar reason. The anions of the normal leuco (or



(X)



(XI)

dihydro) derivatives of flavanthrone and pyranthrone are constituted as (X) and (XI),[120] so that an oxygen atom and a nitrogen atom in flavanthrone, in contrast to two oxygen atoms in pyranthrone, are involved in the reduction process. Thus the semiquinone ion of pyranthrone is stabilized by resonance between equivalent structures in which the odd electron is on one or other of the two oxygen atoms, while the two structures contributing to the resonance of the semiquinone ion in the case of flavanthrone are not equivalent since in one the odd electron is on an oxygen atom and in the other on a nitrogen atom. Although qualitative evidence of semiquinone formation during the oxidation of the normal leuco compound has been obtained in both cases,[120] it is very probable that the semiquinone ion of pyranthrone has considerably greater stability.

By carrying out a potentiometric titration in which potassium ferricyanide solution is added to a buffered solution containing cotton dyed with a vat dye, subsequently reduced on the fiber by means of a slight excess of hydrosulfite, the redox potential of the system at a desired pH can be determined,[121] although there are obvious experimental difficulties. From the data obtained for the redox potentials as the reduced dyeing is progressively oxidized, each dye can be assigned a characteristic potential (E_c), which has been determined for a number of vat dyes. An indication of the light-tendering activity is obtained when E_c is determined with the system in the dark and under illumination; with inactive dyes there is little or no change while there is a significant change with active dyes. The more active the dye, the larger is the change in E_c. By determining the change in E_c at a higher pH (e.g. 12.6), the activity of the dye on cotton in presence of alkali can also be forecast.[121] The experimental procedure, however, is apparently not easy to duplicate, since Turner[70] has stated that Hadfield obtains the same characteristic potential in the dark and under illumination.

By studying the absorption spectra of substances such as tetraphenylhydrazine, oxazine, thiazine and the leuco derivative of Methylene Blue in a "rigid" solvent (e.g., a mixture of ether, isopentane and alcohol at about 90°K), Lewis[122] has found that a molecule may be dissociated by light into two radicals, into positive and negative ions, and into a positive ion and an electron. Thus the ejection of an electron by a molecule of triphenylamine results in the formation of a free-radical ion ($Ph_3N + h\nu \rightarrow Ph_3N^+ + e$).[122] In some cases the last type of dissociation or photooxidation gives semiquinones identical with those obtained by Michaelis by chemical oxidation. The action of light on a solution of a fluorescent dye and a reducing agent can result in the dye being bleached or in the reversible or irreversible oxidation of the reducing agent. Electron transfer mechanisms have been suggested to explain the primary chemical reactions.[123] The photochemical activity of certain grades of zinc oxide has been correlated with the fact that they show no fluorescence in visible light at room temperature when irradiated with ultraviolet light; and it has been suggested that the high-energy portion of the solar radiation is utilized as photochemical energy, while it is dissipated as lower-energy radiation in the grades of zinc oxide which show a strong yellow fluorescence.[124] In view of the complex relationships between fluorescence and photosensitization,[125] it will be of interest to study the fluorescence of the active vat dyes in presence of cellulose.

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[121] Waly, Preston, Scholefield, and Turner, *J. Soc. Dyers Colourists* **61,** 245 (1945).

[122] Lewis and Lipkin, *JACS* **64,** 2801 (1942); Lewis and Bigeleisen, *ibid.* **65,** 2424, 2426 (1943).

The foregoing review will indicate that with the limited data available it is not possible to trace a relationship between the chemical constitution of the anthraquinonoid vat dyes and their activity as catalysts for the photochemical degradation of cellulose, or to arrive at a final conclusion about the mechanism of the reactions. There is need for the accumulation of further data on the activity of an extensive series of chemically pure dyes of known constitution, and on other properties of the dyes, such as the absorption spectra, fluorescence radiation, redox potentials, and semiquinone formation.

[123] Weiss, *Trans. Faraday Soc.* **42,** 133 (1946); Evans, *ibid.* 101.

[124] Winter, *Nature* **163,** 326 (1949).

[125] Franck and Livingston, *J. Chem. Phys.* **9,** 184 (1941).

CHAPTER XLI

CHEMICAL CONSTITUTION OF DYES IN RELATION TO SUBSTANTIVITY

The tendency of a textile fiber to absorb a dye from aqueous solution and to retain it is the basis of normal dyeing processes.[1, 1a, b] The nature of the phenomenon of dye absorption or the "substantivity" of dyes is of theoretical interest and technical importance, but it has not received the attention it deserves. The need is for much wider experimental investigation and for the accumulation of an adequate volume of accurate data on the absorption of dyes of various types by the natural and synthetic fibers. The chemical constitution and fine structure of the fiber, the chemical constitution of the dye and the structure of the aqueous solution, and the influence of added substances and of the conditions of the dyeing treatment have all to be taken into account in studying the mechanism of dyeing. In view of the physical and chemical differences between the different fibers (such as cotton, viscose, cellulose acetate, wool and nylon), and the wide variations in the constitution and properties of the numerous dyestuffs which are now available, it is clear that no single theory of dyeing can cover all dyeing processes. A full discussion of the subject, especially of physico-chemical aspects,[1, 1a] is outside the scope of this book, and the present review is mainly concerned with the structural features of dye molecules which appear to be associated with substantivity for cotton[2] and wool as representing the two major types of cellulose and protein fibers.

Substantivity is not an absolute property and it is difficult to define quantitatively. There is no sharp demarcation between substantive and unsubstantive dyes. Ruggli[3] adopted a method by which, employing arbitrary standards, the substantivity may be stated numerically.

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[1] For a recent account of the theory of dyeing, see Valko, Physical Chemistry of Dyeing in Alexander's Colloid Chemistry, Vol. VI, Reinhold, New York, 1946.

[1a] See also Vickerstaff, The Physical Chemistry of Dyeing, Oliver and Boyd, London, 1950.

[1b] See also Meggy, Developments in the theory of dyeing, *J. Soc. Dyers Colourists* **66**, 510 (1950).

[2] Cf. Venkataraman, Presidential Address, Chemistry Section, Indian Science Congress, 1945.

[3] *J. Soc. Dyers Colourists* Jubilee Vol. 77 (1934).

The absorption is first measured under standard conditions, and then the desorption or "stripping" as the quantity of dye removed by a standard washing treatment. The substantivity is stated as absorption *minus* stripping, both expressed as percentages of the initial quantity of dye in the dyebath. The Ruggli procedure is arbitrary and unsuitable for any attempt at a fundamental interpretation, since dyeing is a reversible process and desorption by a washing treatment introduces an additional and irrelevant complication. The reversibility of the dyeing process has been proved in several ways, and the migration of a dye from the heavier dyed parts of a fibrous material to the lighter dyed parts results ultimately in uniform dyeing; the migrating power of a dye is therefore an important property and its assessment is one of the tests to which dyes are usually submitted. For a comparison of the substantivities of a series of dyes, the requirement is to measure the absorption under well-defined and carefully controlled conditions,[4] and to represent the results as adsorption isotherms; substantivity can then be estimated in terms of a thermodynamic treatment of the dyeing equilibria. The affinity or substantivity of a dye can be defined as the free energy change when a dye is absorbed by a fiber under equilibrium conditions; "affinity" or "substantivity" is also used loosely for practical purposes as indicating the quantity of dye absorbed under practical conditions of dyeing when equilibrium may not have been attained. Physico-chemical studies of dyeing also include measurements of the rate of dyeing, which is dependent on the activation energy of the process.

It is important to work with specimens of dyes of analytical purity; because little attention was paid until 1930 to this obvious need, the earlier investigations lose much of their significance. Commercial direct cotton dyes vary from 20 to 70% in their dye content; higher purity is unusual, but concentrations even lower than 20% may be encountered. The common diluents, present in the dye when it is manufactured or added for standardization and for improving the solubility, are sodium chloride, sulfate and carbonate. In view of the sensitivity of colloidal systems to impurities, especially electrolytes, it is necessary that the dye should be freed completely from these inorganic salts and also from organic intermediates and by-products.[5]

Ionization in aqueous solution is a characteristic of dyes which have affinity for cotton, wool and silk. In direct cotton dyes and acid dyes, which are usually sodium salts of sulfonic acids, the color is in the anion. The leuco derivatives of vat dyes in alkaline solution, sulfur dyes in sodium sulfide solution, and the alkaline solutions of the phenolic or enolic components used for azoic dyeing, are all ionized. Basic dyes are "onium" salts in which the color is in the cation. Wool and silk have affinity for the anions of acid dyes and the cations of basic dyes. It is very probable that cotton absorbs the anions of direct dyes, and not the dye molecules as a whole; but when dyeing has been completed the dye is present on the fiber as the neutral sodium salt.

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[4] Neale, *J. Colloid Sci.* **1,** 371 (1946).

[5] For methods, see Chapters XI and XLII.

Cotton, wool and other textile fibers are composed of linear polymers of high molecular weight. The long macromolecules are held together in bundles or micelles in roughly parallel formation, but in addition to these regions of crystalline character, there are amorphous regions which also consist of the same long chain molecules. The general picture of the dyeing process is somewhat similar for all the fibers, except in the final stage of the mode of attachment of dye to fiber—a difference which will be anticipated from the difference in the chemical constitution of cotton, wool and other fibers. When a fiber, freed from hydrophobic constituents, is placed in water, it is wetted, water is absorbed, and the osmotic pressure swells the fiber. Dealing with an aqueous solution of a dye, the degree of wetting and absorption will depend on the nature of the dye and the fiber, as well as the temperature. X-Ray analysis of swollen fibers has shown that the crystalline orientation of the chain molecules in micelles remains unaltered, so that the water mainly enters the amorphous intermicellar regions.[6] Pores and channels are thus formed in the intermicellar material, the diameters of the pores being of the order of 20–100A; these are large enough to permit the entry of dye molecules, which diffuse along the channels and are adsorbed by the cellulose molecules in the intermicellar regions in such a manner that uniform dyeing results, as indicated by the appearance of the dyed fiber under the microscope. The final stage in the dyeing process must be some kind of combination between fiber and dye, and this has to be considered separately for cotton and wool.

An analogy may be drawn[3] between substantivity to textile fibers and physiological action in their relationship to chemical constitution, although there is an infinitely greater degree of specificity in the physiological action of organic compounds. Discussing molecular structure and biological specificity in connection with the phenomena of immunology, Pauling[7] has stated that the principal forces of attraction which are operative between antigens and antibodies are "the general van der Waals forces (electronic dispersion forces), the forces described as hydrogen-bond forces, and the electrostatic forces between positively charged and negatively charged ionized groups." The forces of attrac-

[6] Katz, *Physik. Z.* **25**, 321 (1924).

[7] XI International Congress of Pure and Applied Chemistry, 1947.

tion between dyes and fibers may be similarly described with the qualification that in cellulose fibers the electrostatic forces between ionized groups are operative only in so far as the hydroxyl groups have some ionic character.

CONSTITUTION OF CELLULOSE[8–11]

Cellulose is present in plants as a skeletal substance, and it occurs in very pure form in the cotton fiber. After careful purification by removal of all extraneous matter, it has the empirical formula of a hexose anhydride, $C_6H_{10}O_5$. Its physical and chemical properties show that it is a high polymer. It is insoluble in ordinary solvents, dissolving only in a few special solvents such as aqueous solutions of cuprammonium hydroxide, calcium thiocyanate and dibenzyldimethylammonium hydroxide, which have a swelling action on the fibrous substance. The size of the molecules varies within wide limits, not merely in cellulose isolated from different sources, but even in the same sample prepared for instance from cotton fibers. Molecular weights, determined by the chemical end-group method and by various physical methods, such as Staudinger's viscosity method or Kraemer's analysis of sedimentation equilibria in the ultracentrifuge, vary from about 100000 to twenty times this figure; stated as the degree of polymerization (D.P.) which is the value of n in $(C_6H_{10}O_5)_n$, the variation is from about 600 to 10000. The D.P. of cellulose in cotton fiber with primary walls only and with secondary walls has been stated to be of the average value of 5940 and 10,650 respectively.[11] Quantitative studies of the behaviour of cellulose must therefore be regarded as yielding results which relate to an average of a molecular species. Acid hydrolysis of cellulose gives a nearly quantitative yield of glucose, which is obviously the fundamental molecule from which the cellulose macromolecule is built up. By acetolysis (the action of acetic anhydride and sulfuric acid), an intermediate product, the disaccharide cellobiose, can be obtained as the octaacetate in 40% yield. Cellobiose is a β-4-glucosido-glucose, and cellulose is a polysaccharide in which a long series of glucose units are linked together in a chain in the same manner as in cellobiose.[12] All the known properties and characteristics of cellulose, including the X-ray diagram,[13] are in agreement with this chain structure.[10] The models proposed for cellulose by

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[8] Ott, Cellulose and Cellulose Derivatives, Interscience, New York, 1943.

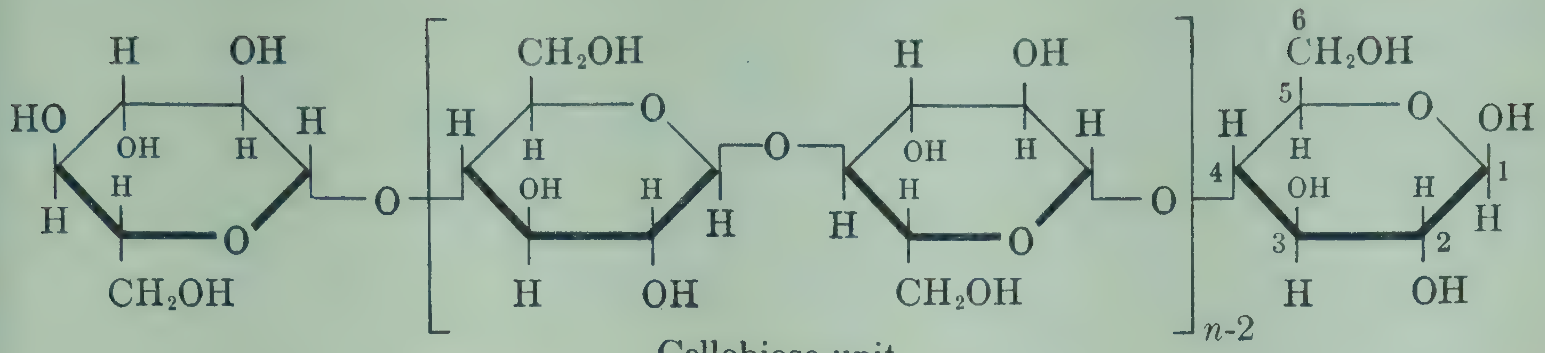
[9] Hermans, Physics and Chemistry of Cellulose Fibers, Elsevier, Amsterdam, 1949.

[10] See also Chapter VI.

[11] Hessler, Merola and Berkley, *Textile Research J.* **18**, 628 (1948).

[12] Haworth, *Helv. Chim. Acta* **11**, 534 (1928); Freudenberg and Braun, *Ann.* **460**, 288 (1928); **461**, 130 (1928).

[13] Mark and Meyer, *Ber.* **61**, 593 (1928).



Cellobiose unit

The cellulose chain

Haworth and by Meyer and Misch[14] are illustrated in Figs. 1 and 2. Fig. 3 represents two views of an atom model of cellulose,[15] which indicate the close packing of the atoms, the steric hindrance around the oxygen bridges, and the non-planar configuration of the molecule.

The chemical reactivity of cellulose towards dye molecules must be associated with the hydroxyl groups, rather than the glucosidic oxygen atoms, the former being much more readily accessible. The loss of affinity for direct cotton dyes when cellulose is converted into an ester such as the acetate is an indication of the part played by the hydroxyl groups in the attachment of dyes to cellulose. Using the technique employed by Klotz, Walker, and Pivan[16] for protein solutions, Preston[17] has examined the ability of various water-soluble polymers containing hydroxyl and ether groups (e.g., methyl cellulose, polyvinyl alcohol, and the polyethylene oxide product, carbowax) to combine with direct dyes by placing the polymer solutions in a collodion bag immersed in the dye

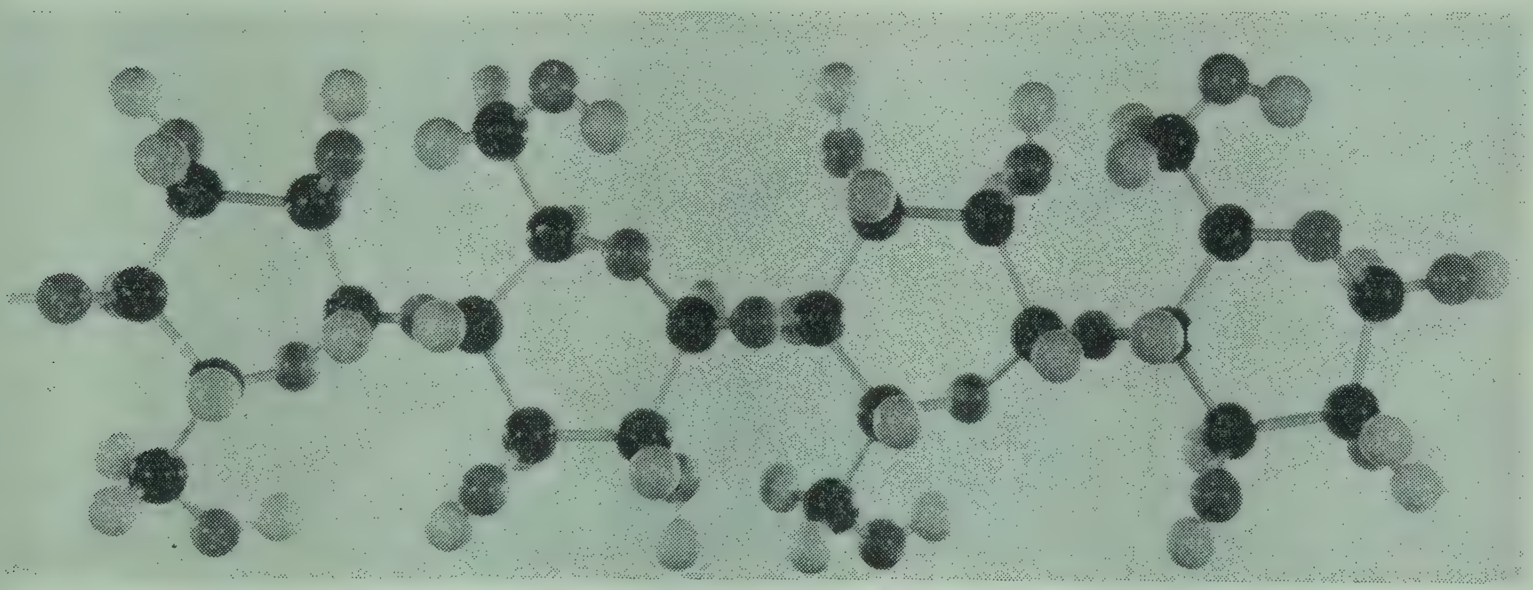


Fig. 1. Cellulose model (Haworth). (By courtesy of Dr. Emil Ott, Hercules Powder Co.)

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[14] *Helv. Chim. Acta* **20,** 232 (1937); *Ber.* **70,** 266 (1937).

[15] Ott in "The Chemistry of Large Molecules," Interscience, New York, 1943, p. 250.

[16] *JACS* **68,** 1486 (1946).

[17] Marshall and Peters, *J. Soc. Dyers Colourists* **63,** 446 (1947). See also Peters and Vickerstaff, *Proc. Roy. Soc. London* **192A,** 292 (1948).

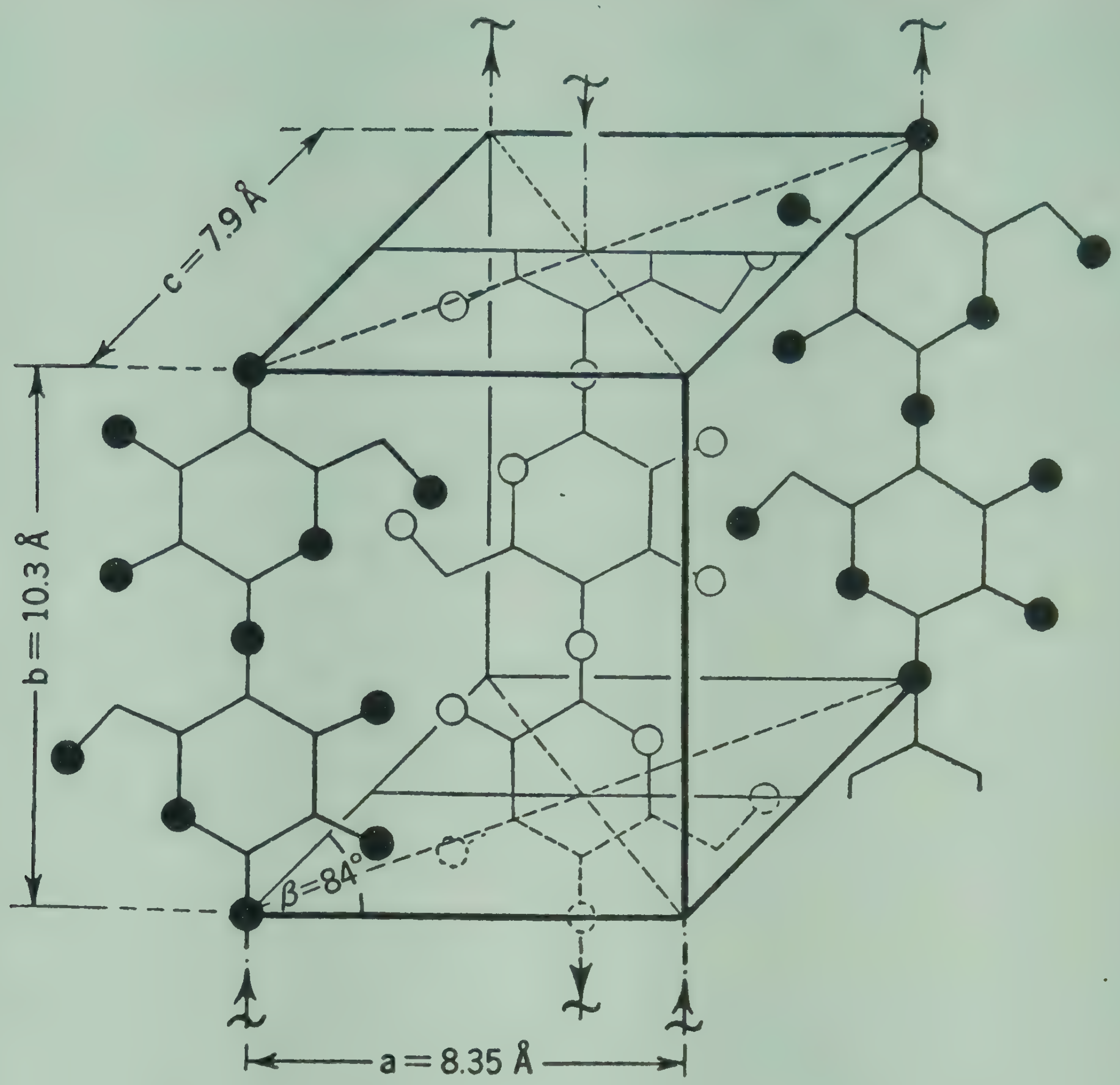

Fig. 2. Cellulose model (Meyer and Misch).

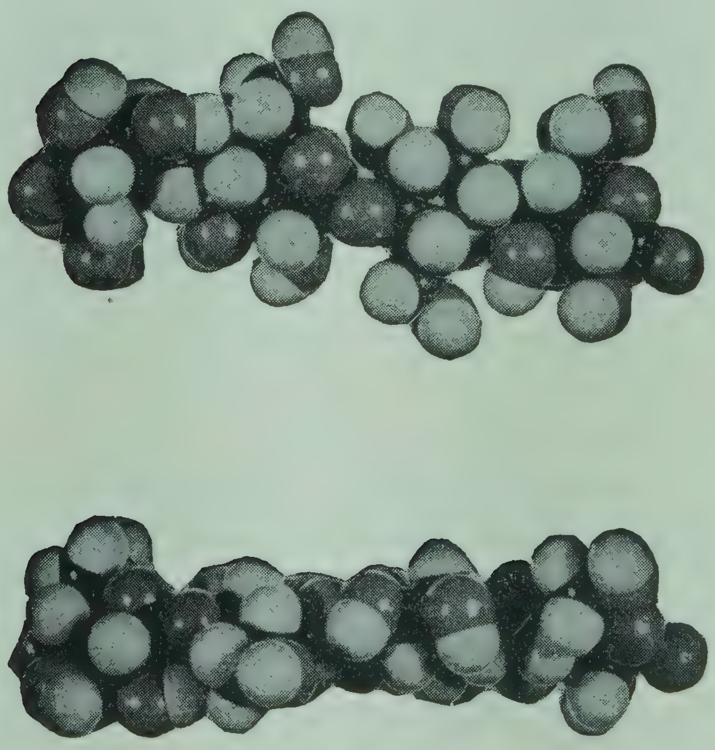

Fig. 3. Views of an atom model of cellulose (Ott).

solution. Preston thus obtained evidence of the combination of direct dyes with compounds containing hydroxyl groups, but not with ethers; and he suggested that hydrogen bond formation between direct dyes and cellulose involves the hydroxyl groups, and not the glucosidic oxygen atoms, in the cellulose molecule. An inspection of the cellulose chain shows that, apart from the two end members, each of the recurring β-glucose units contains one primary alcoholic group and two secondary alcoholic groups. The relative susceptibility of the primary and secondary alcoholic groups in the cellulose chain to attack by reagents varies with the nature of the reagent and the conditions of the reaction.[17a] The hydroxyl groups at positions 2 and 3 of each glucose unit apparently react with cuprammonium to form a soluble complex.[18] When β-glucopyranose units are oriented in a Sachse strainless arm-chair form,[19] the angle between the 2,3-hydroxyl groups permits complex formation.[18] In some reactions there is evidence of the greater accessibility of the primary hydroxyl.[20] The primary alcoholic groups are considered to be mainly responsible for the initial sorption of water (up to 10% R.H.) by cellulose.[21] Among the simple alcohols, it is known that esterification with acid anhydrides is fastest with primary alcohols. The primary hydroxyls in cellulose are esterified most rapidly by *p*-toluenesulfonic acid, the 2- and 3-hydroxyls being attacked less readily in the order named;[20] the nitration of cellulose in carbon tetrachloride in presence of nitrogen tetroxide yields a mononitrate in which the nitration appears to be substantially limited to the primary hydroxyl.[22] Any degradation of cellulose in which there is a shortening of the molecular chain would be expected to influence the dye absorption as a result of the change in the fine structure and the colloid-chemical properties of the fiber; but even when cellulose is submitted to oxidations in which some of the primary alcoholic groups are converted into aldehyde or carboxyl groups, without a significant change in the chain length, there is a marked decrease in the affinity of dyes for cellulose. Carefully purified cellulose contains a small number of carboxyl groups, formed probably by oxidation of the potential aldehyde group at one end of the chain, and the dyeing properties of native cellulose depend to some extent on the carboxyl content; but when a few of the primary alcoholic groups are oxidized to carboxyl groups, there is a profound effect on dye absorption. Using nitrogen dioxide as the oxidizing agent, Kenyon[23] has achieved the preparation of an oxycellulose in which cellulose retains its fibrous structure and oxidation is confined mainly to the primary alcoholic groups. Kenyon's oxycellulose is devoid of affinity for direct cotton dyes. However, the dye affinity of acidic oxycelluloses of other types (e.g., periodic acid-chlorite oxycellulose containing carboxyl groups in the 2,3-positions)[24] will have to be examined systematically before conclusions can be drawn.[25]

[17a] See also Heuser, *Textile Research J.* **20,** 828 (1950); Timell, *Svensk Papperstidn.* **52,** 107 (1949); Sönnerskog, *ibid.* **51,** 50 (1948).

[18] Reeves, *JACS* **71,** 212 (1949); *Science* **99,** 148 (1944).

[19] Peirce, *Nature* **154,** 398 (1944); Astbury and Davies, *ibid.* 84.

[20] Mahoney and Purves, *JACS* **64,** 9, 15 (1942). See also Heuser, Heath and Shockley, *JACS* **72,** 670 (1950).

[21] Purves *et al.*, *JACS* **66,** 66 (1944).

[22] Kenyon *et al.*, *JACS* **69,** 355 (1947).

[23] Kenyon *et al.*, *JACS* **64,** 121 (1942) *et seq.*

CELLULOSE FIBER STRUCTURE

An important characteristic of the cell walls of cellulose fibers is their submicroscopic porosity, shown for instance by the fact that the density of the cotton fiber (1.05), calculated from the microscopically measured fiber volume, is about 30% less than the density (1.55 or more) determined by the buoyancy method.[9] When a fiber is placed in water, it undergoes lateral swelling (about 25% for cotton and 50–70% for viscose), while the length remains practically unaltered (the lengthwise swelling being about 1% for cotton and 2–5% for viscose); in this property of swelling, as well as other properties such as optical behavior, the fiber is anisotropic.[26] Cellulose fibers contain channels which are large enough to permit the entry of dye molecules, but the diffusion of a dye into the fiber is facilitated by swelling, and the rapidity of the entry is dependent on the degree of swelling and on the size of the dye molecule. It is not possible by the X-ray method to determine the width of the vacuoles in a fiber, and estimates have only been obtained indirectly. From a study of the moisture relations of cotton, the diameter of the smallest pores has been found to be of the order of 13A.[27] By determining the rate of flow of water through viscose membranes, the pore diameter in viscose in the unswollen state has been estimated to be less than 5A, but this increases to 20–30A by normal swelling, and to 100–150A by swelling in caustic soda solution. Dye molecules can penetrate the capillaries only in the swollen state.[28] In most of the experimental work on the theory of dyeing cellulose, regenerated cellulose sheets have been employed; and by studying the distribution of water it has been calculated that the average diameter of the pores traversing the sheet is 40 to

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[24] Nevell, *J. Textile Inst.* **39,** T118 (1948); Rutherford, Minor, Martin, and Harris, *J. Research Natl. Bur. Standards U.S.* **29,** 131 (1942).

[25] See also Neale and Stringfellow, *J. Soc. Dyers Colourists* **56,** 17, 21 (1940).

[26] For an account of the submicroscopic structure of cell walls, see Frey-Wyssling, *Science Progress* **34,** 249 (1939).

[27] Urquhart and Williams, *J. Textile Inst.* **15,** T433 (1924); see also Frey-Wyssling, *Kolloid-Z.* **85,** 148 (1938). Nitrogen-sorption measurements of cotton linters soaked in cold 10% sodium hydroxide solution indicate a maximum pore diameter of 40A and a surface area as great as 71.3 m.^{2}/g.; Hunt, Blaine and Rowen, *Textile Research J.* **20,** 43 (1950).

[28] Morton, *Trans. Faraday Soc.* **31,** 262 (1935).

60A.[1,29] The pore dimensions in viscose fibers, calculated from data on equilibrium dye absorption and on double refraction, are of the order of 30–50A.[30,31] It would appear that in natural cellulose fibers there are at least a few submicroscopic spaces as large as 100A, since X-ray analysis of fibers in which colloidal gold and silver are deposited in the cell wall has revealed diameters of about 100A for the metal particles.[32]

The chain molecular structure of cellulose, deduced by chemical evidence, has been confirmed and amplified by X-ray analysis.[8,15] The calculated length of the cellobiose unit is about 10.3A, while the X-ray fiber diagram indicates a repeating pattern at the identical intervals. The picture that emerges from the X-ray diffraction photographs is a digonal screw arrangement, for which the cellobiose unit, with its lower half rotated through 180°, permits the necessary 1,4-linkages. The distance of 10.3A at which the pattern repeats, representing for instance the distance between two primary alcoholic groups on the same side, is important in determining the structure of dyes which can attach themselves to the cellulose chain. The crystallinity of cellulose varies with the source and with the treatment to which the material has been submitted. A high degree of crystallinity is found in the natural fibers, the cellulose chains being deposited in roughly parallel formation with reference to the fiber axis. In the crystal structure proposed by Meyer and Misch,[14] the chains run alternately in opposite directions, and the adjacent chains are held together by hydrogen bonding.[33] Native cellulose and hydrated or mercerized cellulose exist in two crystalline modifications, and the two forms are interconvertible and chemically identical. Mercerized cellulose has greater adsorptive power, because of decrease in crystallinity.

The crystallites or micelles in the fiber are long in the direction of the fiber axis and relatively narrow in the perpendicular direction; the length of the crystallites of ramie is at least 600A corresponding to a chain length of well over 100 glucose units, and the width is about 55A corresponding to 100–200 cellulose chains; the micelle sizes for viscose are of the order of 350A × 40A.[34] The fiber, however, is not composed entirely of these crystallites, and it is clear from the X-ray evidence that the crystallites are embedded in amorphous or disordered regions. A given molecular chain can go through a crystalline region, enter and go

[29] McBain and Kistler, *Trans. Faraday Soc.* **26,** 157 (1930).

[30] Preston and Kapadia, *J. Soc. Dyers Colourists* **63,** 434 (1947).

[31] Preston, Mhatre, and Narasimhan, *J. Soc. Dyers Colourists* **65,** 17 (1949).

[32] Frey-Wyssling, *Protoplasma* **27,** 372 (1937).

[33] See, however, Hermans, *Kolloid-Z.* **102,** 169 (1943).

[34] Hengstenberg and Mark, *Z. Krist.* **69,** 271 (1928).

through a disordered phase, and enter a second crystallite (Fig. 4).[35] We thus have a continuous transition between crystalline and disordered regions. Since the reactivity of cellulose is mainly in the amorphous regions, attempts have been made to evaluate the crystalline-amorphous ratio in a fiber by various methods. However, definitions of crystalline and amorphous regions are not rigid, since intermicellar material is not entirely in random order.

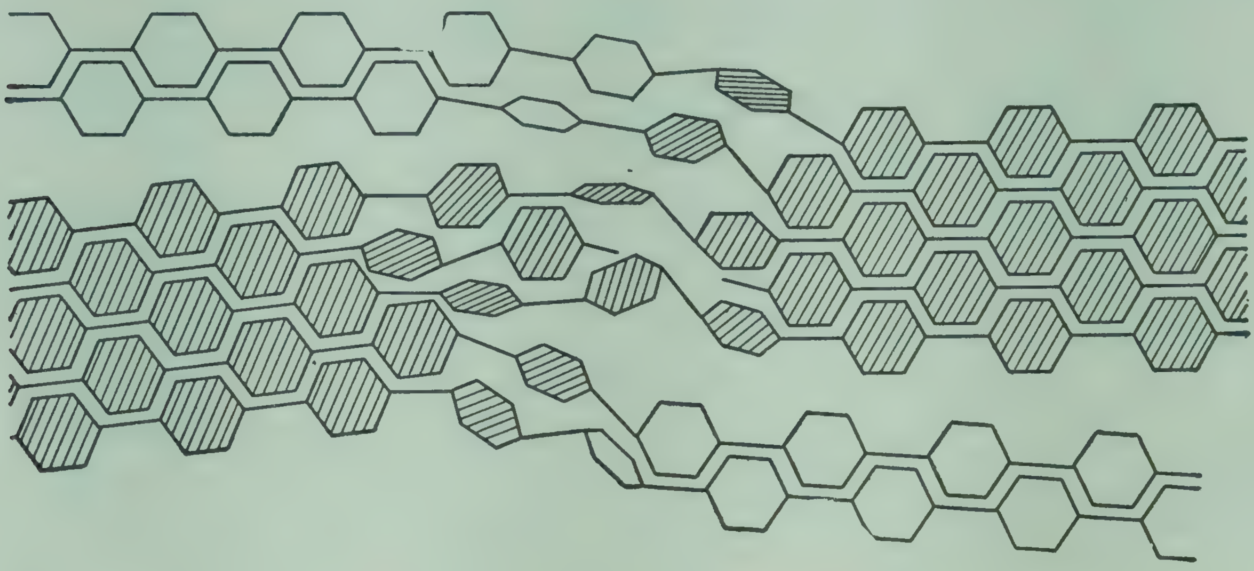

Fig. 4. Sketch of cellulose chains which belong partly to crystallites and partly to disordered areas (Mark).

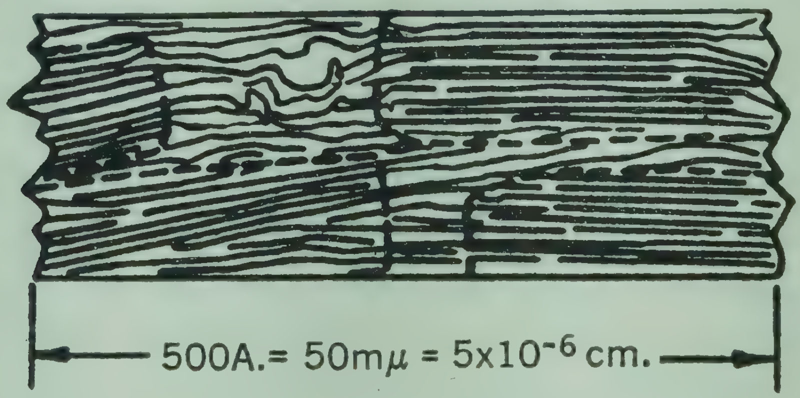

Fig. 5. Fine structure of cellulose (Mark).

Cellulose is highly hydrogen-bonded, and these bonds provide the cross-linkages which determine the fine structure of the fiber. The crystallinity of the fiber and the extent of hydrogen-bondedness are interrelated. In the ramie fiber most of the hydroxyl groups are involved in hydrogen-bonding.[36] Although the disorderly regions of a cellulose

[35] Mark in the Chemistry of Large Molecules, Interscience, New York (1943). See also Ward, Jr., *Textile Research J.* **20,** 6 (1950). Howsmon, *ibid.* **19,** 152 (1949), has attempted to determine the "accessibility" and "crystallinity" of cellulose fibers from moisture regain data. Frilette, Hanle, and Mark, *JACS* **70,** 1107 (1948), have used hydrogen-deuterium interchange between cellulose hydroxyls and D_2O for this purpose.

[36] Ellis and Bath, *JACS* **62,** 2859 (1940).

fiber are also hydrogen-bonded structures, it is clear from the difference in the reactivity of the micellar and intermicellar regions towards water, alkali, acid, dyes and other reagents that there is a difference in the number and stability of the hydrogen bonds in these regions. Treatment with alkali under mercerizing conditions results in the opening of hydrogen bonds throughout the fiber; the moisture regain and the absorption of dyes are increased, and both these effects are due to the greater accessibility of hydroxyl groups in mercerized cotton. In a dyeing process, relatively few of the hydrogen bonds are broken, and these are confined to the cellulose molecules in the disordered regions and perhaps to an outer sheath of the bonded hydroxyl groups in the crystalline phase of the fiber. Some of the intercellulosic hydrogen bonds are replaced by hydrogen bonds between cellulose and dye. Several considerations show the extreme improbability of dye molecules penetrating the crystallites, breaking some of the hydrogen bonds holding the chains together and replacing them by new hydrogen bonds between cellulose and dye. The X-ray diagrams of dyed cotton and regenerated cellulose show that dyeing has no influence on the fiber structure.[1]

The importance of the hydrogen bond in dyeing is indicated by the fact that all dyes contain nitrogen and/or oxygen; the availability of the unshared electrons of these atoms in amino, azo, hydroxyl, carbonyl, amide and other groups largely determines the affinity of dyes for cellulose. The substantivity of a dye is therefore primarily related to the number and strength of the hydrogen bonds in which it can be implicated, but to enable the dye molecules to reach the sites in the cellulose structure at which they can be held, the dye has to fulfil certain requirements of shape and size.

The benzidine type of direct cotton dye possesses a flat elongated structure, and the dichroic behavior of fibers dyed with such dyes shows that the dye molecules are probably disposed with their long axis parallel to the long axis of the cellulose chains,[37, 38, 39] although the dye molecules apparently diffuse into the fiber only perpendicular and not parallel to the fiber axis, as shown by an examination of fibers embedded in a hydrophobic medium so that the fiber ends permit free access to the dye solution.[40] Further, cellulose fibers, which have been stained with

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[37] Ambronn and Frey, Das Polarisationsmikroskop, Akad. Verlag, Leipzig, 1926.

[38] Boulton and Morton, *J. Soc. Dyers Colourists* **56,** 145 (1940).

[39] Okajima *et al., J. Soc. Chem. Ind. Japan* **49,** 38, 128 (1946). Morey, *Textile Research* **3,** 325 (1933); **4,** 491 (1934); **5,** 105, 483 (1935), has used the polarization of fluorescent light from dyed fibers to measure at one time the average orientation over hundreds of cotton fibers. He has also used the dichroism of dyed fibers for studying micellar arrangement.

[40] Frey-Wyssling, *J. Polymer Sci.* **2,** 314 (1947).

iodine or filled with a colloidal deposit of gold and silver, also exhibit dichroism.[37] The degree of orientation in cellulose has been determined by measurements of the dichroism.[41] Rates of dyeing of viscose increase with the available surface and decrease with the degree of orientation. The orientation of the cellulose molecules in viscose rayon fibers affects both the rate of dyeing and the equilibrium uptake.[30, 42]

From the saturation absorption value for Sky Blue FF on bleached cotton, taken as 6% although an exact upper limit cannot be defined, it has been calculated[25, 43] that the area of the available absorbing surface of cellulose is 1.5×10^6 cm.^{2}/g. on the assumption that the dye is absorbed in a monomolecular layer and that the area occupied by one molecule of dye lying flat is 400 sq. A.

Cellulose and Direct Dyes[1, 1a, 44]

Many attempts have been made in recent years at mathematical and thermodynamic analyses of the direct dyeing of cellulose. Dyeing equilibria and dyeing kinetics are problems of the utmost complexity, but by arbitrary simplifications of the system mathematical treatment has been possible and considerable progress has been made in deriving quantitative relationships between the various factors involved in the absorption of direct dyes by cellulose. On the other hand, the generally unsatisfactory position of dyeing theories is indicated by their complete lack of application to cellulose dyeing practice. From both the theoretical and practical points of view, cellulose presents more complicated dyeing problems than wool and silk.

The character of aqueous solutions of direct cotton dyes as true or colloidal solutions has been much debated. Until recently the explicit view was that direct dyes form colloidal solutions, the size of the aggregates of a given dye depending on temperature and salt addition; it was considered that molecularly dissolved particles diffused freely through the fiber and took no part in the dyeing operation unless the conditions were subsequently modified (e.g. by adding salt) in order to effect a change in the state of aggregation. Robinson[45, 46] has investigated the structures of aqueous solutions of direct cotton dyes by several methods, such as osmotic pressure, diffusion, conductivity, and transport number measurements, and has obtained definite evidence of aggregation. It is reasonable to expect that the structural factors which enable a dye molecule to be strongly adsorbed on cellulose would also be favorable to aggregation in aqueous solution, and the real problem is to make a quantitative assay of the degree of aggregation of a given dye under the conditions employed in the dyeing process. Evidence for the aggregation of Sky Blue FF has been obtained by conductivity measurements.[44, 47] The dye forms blue solutions in water and in solutions of cationic soaps above the critical concentrations for micelle formation; below the critical concentration, the solution is reddish, and the color change is sufficiently sharp for determining the end point when a soap solution containing the dye is titrated against a solution of the dye in water. The extent of aggregation of Sky Blue FF in the absence of salts is unknown. Valko has assigned an aggregation number of 3.7 to dye solutions of 0.002 to 0.02% concentration in presence of 0.02 to 0.05 molar sodium chloride.[1] Measurements of the sedimentation equilibria indicate that Congo Red solutions are monodisperse and the molecular weight of the dye in 0.1N sodium chloride solution is between 8000 and 9000, corresponding to about 12 molecules.[48] The dye Bordeaux COV (benzidine $\rightrightarrows$ two moles β-naphthol-8-sulfonic acid) is almost molecularly dispersed, while Benzopurpurine 4B aggregates readily.[45] The degree of aggregation and the mean particle size increase with salt concentration (see Fig. 6), and decrease with temperature; the decrease in aggregation with increase in temperature shows that it is an exothermic reaction. Considering the dyes which have the requisite substantivity for practical dyeing, it would appear that about 90% of most of the dyes is in molecular solution at the temperature of dyeing.

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[41] Preston, *J. Soc. Dyers Colourists* **47,** 312 (1931); *J. Soc. Chem. Ind.* **50,** T199 (1931). Preston and Su, *J. Soc. Dyers Colourists* **66,** 357 (1950), have studied the relation between the degree of orientation of dyed regenerated cellulose fibers and the degree of polarization of their fluorescence under various conditions. They have shown that the fluorescence method gives a measure of the dichroism of the dyed fibers.

[42] Preston and Pal, *J. Soc. Dyers Colourists* **63,** 430 (1947).

[43] Paneth and Radu, *Ber.* **57,** 1221 (1924). See also Howell and Jackson, *JCS* 979 (**1937**).

[44] Standing, *Trans. Faraday Soc.* **41,** 410 (1945).

From diffusion rate experiments Valko[49] has calculated the particle size of the leuco compounds of five vat dyes in a solution prepared from the dye (0.1 g.), hydrosulfite (0.05 g.), sodium hydroxide (0.1 mole) and sodium chloride (0.2 mole) per l. (Table I). Similar figures were obtained for the particle sizes of a few Indigosols. On the average three dye ions

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[5] Robinson *et al.*, *Proc. Roy. Soc. London* **131A**, 576 (1931); *ibid.* **143A**, 630 (1934); *ibid.* **148A**, 681 (1935); *Trans. Faraday Soc.* **29**, 352 (1933); **35**, 771, 780 (1939).

[6] See also Valko, *Trans. Faraday Soc.* **31**, 230 (1935).

[7] Holmes and Standing, *Trans. Faraday Soc.* **41**, 568 (1945); Corrin and Harkins, *JACS* **69**, 679 (1947).

[8] Quensel, *Trans. Faraday Soc.* **31**, 259 (1935).

[9] *JACS* **63**, 1434 (1941).

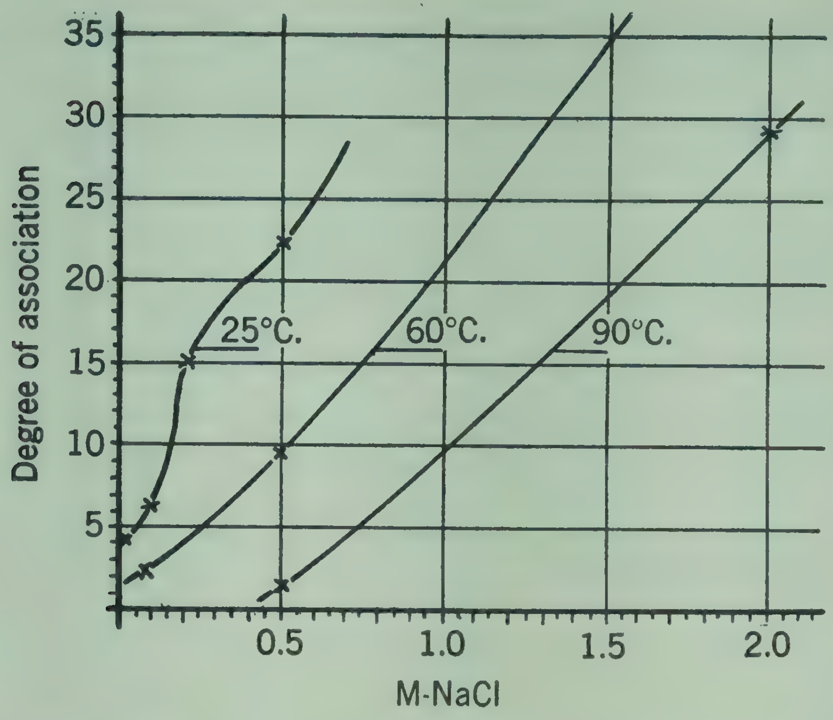

Fig. 6. Degree of association of direct dyes at 25° as a function of the concentration of NaCl. From diffusion measurements (Valko).

aggregate to form an ionic micelle, but it must be assumed that there are enough single ions to penetrate the pores of the swollen cellulose fiber.[50]

TABLE I

Particle Size of the Leuco Derivatives of Vat Dyes at 25°

Dye	*Particle radius A*	*Molecular weight*	*Aggregation No.*
Caledon Jade Green	7.89	1874	3.6
Indanthrene Red RK	7.19	1416	3.8
Indanthrene Golden Yellow GK	6.42	1009	3.3
Indanthrene Golden Yellow RK	6.31	963	2.1
Indanthrene Yellow GK	7.14	1388	3.1

When ramie is dyed from alcoholic solution, in which the aggregation of direct dyes is very improbable, it is optically indistinguishable from ramie dyed in the usual manner from aqueous solution with the addition of salt.[38] Comparing the absorption spectra of a dye in water and on viscose or cuprammonium sheet, λmax. undergoes a bathochromic shift in the dyed materials.[51] The dichroism of a fiber dyed with a direct cotton dye is of the opposite sense to the dichroism of a large elongated dye micelle in aqueous solution.[38] These facts generally lead to the conclusion that direct cotton dyes are at least partly aggregated in aqueous solution, but molecularly dispersed in the fiber.[52] At the temperature of dyeing, the dye is mainly in molecular solution, but in equilibrium with aggregated particles, so that the dye is polydispersed.[53] The pore sizes in the fiber indicate that the dye can effect entry only as single molecules or as small aggregates; and as diffusion proceeds, the aggregates in the solution dissociate until equilibrium between fiber and dye solution has been established.

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[50] See also Moryganov, *Kolloid. Zhur.* **6,** 85 (1940).

[51] Kruger and Rudow, *Ber.* **71,** 707 (1938).

[52] Morton, *J. Soc. Dyers Colourists* **62,** 272 (1946).

It is likely that groups in the dye anion which are responsible for substantivity to cellulose are also responsible for the aggregation of the dye in solution and that substantivity is associated with, but not the result of, the colloidal properties of the dye. The tendency to aggregate in the presence of inorganic electrolytes provides a useful indication of the substantivity of dyes to cellulose.[54]

Direct cotton dyes interact in aqueous solution, and the spectra of the mixtures in water are not additive.[55] When mixtures are used to dye cotton, the absorption of one component, as compared with its absorption when dyed singly, is considerably lower than the value to be anticipated merely from the competition of the two dyes for the available surface. When cotton is dyed with a mixture of a slowly dyeing dye with great affinity for cellulose (e.g. Chicago Blue B) and a rapidly dyeing dye of low affinity (e.g. Chrysophenine G), there is found at all concentrations a decrease in the amount of the former dye adsorbed.[56] Apparently, the displacement of the quickly diffusing dye by the large molecules of the slowly diffusing dye becomes very difficult.

The first quantitative treatment of the dyeing of cellulose with direct dyes is due to Neale.[57] A vital factor in direct cotton dyeing is the use of sodium chloride or sulfate, and the salt effect has been studied and interpreted quantitatively. Cellulose is negatively charged with respect to water; the electrostatic effect of the zeta potential is to oppose the absorption of an anion, and the addition of salt overcomes this repulsion.[58] The presence of carboxyl groups as in some of the acidic oxycelluloses and the adsorption of the dye anion as the dyeing proceeds increase the negative zeta potential. Neale has shown that the basic dyes Janus Red B (CI 266) and Victoria Blue B (CI 729) have a strong affinity for bleached cotton even from a neutral solution containing no added electrolyte, and that the behavior of these dyes is in favor of the electrostatic theory of the salt effect.[59] The dye anions are directly bound to the cellulose chain, and the sodium ions are held by the sulfonic groups so that the entire complex is electrically neutral. One function of salt in the dyeing process is to restrain the tendency of the sodium ions in the dye molecules adsorbed by cellulose to escape into the surrounding water. Another important function of salt is to lower the solubility of the dye in water, since decrease in solubility tends to increase the absorption of the dye. The salt effect varies considerably from dye to dye, and it is dependent on the aggregation characteristics of the dye. Thus, Sky Blue FF (dianisidine $\rightrightarrows$ 2 moles 1-amino-8-naphthol-2,4-disulfonic acid), if it is chemically pure and completely free from inorganic electrolytes, is not absorbed at all by cellulose, which in fact absorbs water preferentially from a solution of pure Sky Blue FF in pure water; but Benzopurpurine 4B (*o*-tolidine $\rightrightarrows$ 2 moles naphthionic acid) is appreciably absorbed from aqueous solution free from electrolytes.[60] Neale suggested a quantitative explanation of the absorption of dyes by cellulose in terms of a Donnan membrane equilibrium, regarding direct dyeing as a process of diffusion in which an ultimate equilibrium between cellulose and dyebath is attained, dependent on the conditions of dyeing. The diffusion of the dye anions from the dyebath to the surface of the fiber, when the solution is in a state of ebullition or mechanical agitation, is instantaneous, and this may also be considered to be true of the final stage of attachment of the dye molecule to the cellulose molecule; the rate-determining step in a dyeing process is the diffusion of the dye from the surface of the fiber into the interior of the water-swollen cellulose.[61] Making a careful study of the effect of time, added salts, dye concentration and temperature on the absorption of dyes by cellulose, Neale observed a rough correlation between the apparent diffusion coefficient and the amount of absorption. When salt was added to the dyebath, the diffusion coefficient increased, reached a maximum and then fell, whereas the absorption at equilibrium steadily increased. The absorption of Sky Blue FF was a reversible process, and the increase in absorption with time was in agreement with the theory of diffusion.

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[53] Rummler, *Spinner u. Weber* **55,** No. 48, 6 (1937).

[54] Lenher and Smith, *Ind. Eng. Chem.* **27,** 20 (1935).

[55] Neale and Stringfellow, *J. Soc. Dyers Colourists* **59,** 241 (1943); see also Lemin and Vickerstaff, *Trans. Faraday Soc.* **43,** 491 (1947).

[56] Jensen, *Kem. Maanedsblad.* **23,** 105 (1942).

[57] Hanson, Neale, and Stringfellow, *Trans. Faraday Soc.* **31,** 1718 (1935).

[58] Neale, *Trans. Faraday Soc.* **42,** 473 (1946); see also Neale and Peters, *ibid.* 478; Gee and Harrison, *ibid.* **6,** 42 (1910).

There has been an increasing realization in recent years of the complexity of the direct dyeing process, and the problem is being studied from new angles, so that more data may become available for an ultimate overall assessment of all the factors. Figures for 50% equilibrium exhaustions, which indicate the diffusion and migration properties of the dyes, have been determined.[62] Another experimental approach is to measure rates of dyeing for a series of dyes at equal salt concentrations;[63] the significance of these data in practical dyeing is that rapid dyeing and leveling power usually go together. A surface potential theory of the effect of salt and temperature on the apparent diffusion coefficient has been proposed, considering the diffusion of dye into a cellulose sheet as a process of activated diffusion with absorption.[64] Making several simplifying assumptions, a diffusion-adsorption equation has been developed for the absorption of direct dyes by cellulose sheet; the equation is partially successful in correlating data obtained at high salt concentration, but fails at low salt concentration.[65] Neale has recently attempted to provide a simple physical picture of the effect of electrical forces on the dyeing process, leaving out of account the short range forces, such as the hydrogen bond, which determine the affinity of a dye for the fiber and the mode of attachment of the two.[66] The electrostatic effect, due to the charges on the fiber and the color ions, is "not the principal factor in the affinity of a dye for a fiber, but the variations in the strength and character of the electrostatic force are responsible for the effects of salt in dyeing, and for the effect of acid on the dyeing of silk and wool."

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[59] *Trans. Faraday Soc.* **43,** 338 (1947).

[60] Neale, *J. Soc. Dyers Colourists* **52,** 252 (1936); Boulton, *ibid.* **60,** 5 (1944).

[61] Boulton *et al.*, *J. Textile Inst.* **24,** 113 (1933); Neale and Stringfellow, *Trans. Faraday Soc.* **29,** 1167 (1933).

The sorption of direct dyes by cellulose, like the aggregation of the dyes in aqueous solution, is an exothermic process, as shown by the decrease in the amount of sorbed dye with increasing temperature. This is true of all the substantive dyes, including those which have little or no tendency to aggregate in solution, and it is clear that molecular forces are involved in the sorption of a dye by cellulose. Using the measurements of Neale[67] on the sorption equilibrium of Chlorazol Fast Red K (aminoazobenzene disulfonic acid → benzoyl-J-acid) on cellophane at 25° and 90°, K. H. Meyer calculated the molecular heat of sorption as 5 kcal. per mole; he considered the value high and supposed that one molecule of the dye entered into association with several hydroxyl groups,[68] but Meyer's calculation was based on inadequate data. The energy changes in dyeing cellulose (cotton, mercerized cotton, cuprammonium and viscose rayon) with direct dyes have been recently examined, adopting a simple thermodynamic treatment of the experimental data on the adsorption isotherms of a series of 14 dyes at temperatures of 50–100°.[17] This treatment of the dyeing equilibrium is applicable to dyes which are not aggregated in solution, and deviation from the behavior to be expected from the theory is regarded as evidence of the presence of aggregates. Two main simplifying assumptions are made. One is that the dyes (Na_zD) are completely dissociated both in solution and on the fiber, the dye anions alone being specifically absorbed by the cellulose, although other ions may be carried into the fiber to produce electrical neutrality. The activity of the dye, both in solution and in the fiber, is represented as the product of the ionic activities assumed to be proportional to the concentrations of the sodium and dye ions; in the fiber the proportionality constant has the dimensions of a reciprocal volume $\left(\frac{1}{V}\right)$. The volume, V, in l./kg. of dry fiber, which may be termed the effective volume of the cellulose phase, is calculated from the absorption data for Chrysophenine G, an unaggregated dye. The values thus assigned to V, in comparison with the figures for moisture absorption[69] and for the amounts of water dissolved in the fiber as distinct from chemically combined water,[70] are stated in Table II.

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[62] Boulton and Reading, *J. Soc. Dyers Colourists* **50,** 381 (1934); Boulton, *ibid.* **60,** 5 (1944).

[63] Lemin, Vickers and Vickerstaff, *J. Soc. Dyers Colourists* **62,** 132 (1946).

[64] Crank, *J. Soc. Dyers Colourists* **63,** 293, 412 (1947); **64,** 386 (1948); **66,** 366 (1950).

[65] Standing, Warwicker and Willis, *J. Textile Inst.* **38,** T335 (1947).

[66] Neale, *J. Soc. Dyers Colourists* **63,** 368 (1947).

[67] Garvie, Griffiths, and Neale, *Trans. Faraday Soc.* **30,** 271 (1934).

[68] Natural and Synthetic High Polymers, Interscience, New York, 1942, p. 274.

TABLE II
VOLUME OF THE CELLULOSE PHASE (l./kg. DRY FIBER)

Fiber	*Moisture absorption*	*Dissolved water*	*Adsorption of Chrysophenine G*
Cotton	0.22	0.16	0.30
Mercerized cotton	0.26	0.21	0.50
Viscose rayon	0.46	0.27	0.45
Cuprammonium rayon	0.37	0.26	0.65

The values (ΔG^0) for the standard change in free energy (the affinity) are calculated from the equation

$$-\Delta G^0 = RT \ln [D_f] \cdot [Na_f]^z - RT \ln [D_s] \cdot [Na_s]^z - (z + 1)RT \ln V$$

in which R is the gas constant; T is the absolute temperature; (D_f), (Na_f), (D_s), and (Na_s) are the ionic concentrations of the dye ions and sodium ions in the fiber and in the solution. It is obvious that the affinity is dependent on the value ascribed to V, especially in comparing dyes of different ionic charge (z). However, the results on different fibers were on the whole in good agreement,[31] and it could be concluded that the affinity of a direct dye was the same for all the fibers examined, and

[69] Urquhart and Williams, *J. Textile Inst.* **15**, T559 (1924).

[70] Hailwood and Horrobin, private communication to Marshall and Peters in ref. 17.

probably for all cellulosic substrates. The affinity of a dye for cellulose was therefore calculated as the mean affinity for the different fibers. By plotting these affinities against temperature, the mean heats of reaction were obtained and the mean entropy changes in dyeing were calculated from the two sets of figures, and are stated in Table III.

TABLE III

MEAN VALUE OF THE HEATS OF DYEING (ΔH) AND ENTROPY CHANGE (ΔS) OF DIRECT DYES ON CELLULOSIC FIBERS FOR A MEAN TEMPERATURE OF 350°K.

Dye	$-\Delta H$ *kcal per mole*	$-\Delta S$ *gcal per °C. per mole*
Chrysophenine G	14	31
Durazol Red 2B	11	21
Durazol Fast Yellow 6G	31	73
Chlorazol Brown M	11	14
Durazol Grey RG	15	31
Chlorazol Violet N	12	21
Chlorazol Fast Scarlet 8B	20	43
Chlorazol Sky Blue FF	22	44

The heat of dyeing represents the energy of bond formation between cellulose and dye, and the entropy change represents the restriction in the mobility of the electrons of the dye molecule as a result of its attachment to the cellulose molecule. The entropy change should increase with an increase in the points of attachment, and therefore with an increase in the heat of reaction, and this is seen to be true from Table III. Taking the heat of formation of a hydrogen bond as 7 kcal, the heat of reaction of water with α-glucose, Marshall and Peters conclude that at least two hydrogen bonds are involved in the attachment of a direct dye to cellulose; but they add that our knowledge of the hydrogen-bonding powers of the various reactive groups in direct dyes is quite inadequate for predicting heats of reaction. It is to be anticipated that the attachment of a dye molecule to cellulose involves hydrogen bonding of different degrees of stability, and therefore of different heats of formation. Although the heat of formation of hydrogen bonds varies with the nature of the bonding groups, the variations are between 4 and 8 kcals, and it is reasonable to postulate a minimum of two hydrogen bonds between a dye molecule and cellulose. The energy released in the absorption of Chrysophenine G, a nonaggregating dye, by cellulose sheet has been calculated to be about 14 kcal per mole of dye adsorbed, a value which is in broad agreement with the view that the union between each dye molecule and cellulose is by means of two hydrogen bonds,[71] although there are no grounds for assuming that the postulated hydrogen bonds are the sole factors in the values calculated for ΔH. The heat of dyeing Sky Blue FF on cotton has been found to be between 17 and 19 kcal.[72] Graham and Fromm find that with decreasing values of the equilibrium sorption the differential heats of dyeing increase from 15.2 to 22.4 kcal/mole of sorbed dye for Calcodur Blue 4GL (the trisazo dye, aniline → Cleve-6-acid → Cleve-6-acid → J-acid);[73] their calculations are made from the variation of absorption with temperature, and not from affinity measurements dependent on a definition of the activity of the dye in the fiber.[17] Graham and Fromm ascribe the variations in the heat of dyeing observed by them to variations in the heat of sorption associated with different portions of the fiber surface, and also suggest the occurrence of multilayer dye sorption.

Surface-activity and substantivity. Common types of wetting agents and detergents have some characteristics which are of interest in a discussion of the chemical constitution of substantive dyes.[74] Wetting agents and detergents are usually colloidal electrolytes, which may be anion-active or, less frequently, cation-active or non-ionic; and the properties of the polar molecules depend largely on the balance between the hydrophobic and hydrophilic constituents. Among the properties of a substance, the possession of which is likely to be favorable to its ability to act as a wetting agent and detergent for textile fibers, may be postulated a certain affinity for the latter.[75] Nonpolar molecules are apparently not absorbed by cellulose,[3] and the polar character of substantive dyes as well as wetting agents and detergents is involved in their sorption on the outer surface of the fiber and subsequent migration to the interior accessible surface.[76] The substantivity of dyes is partly related to the ability of the dye ions to form aggregates or micelles; and in detergents micelle formation sometimes runs parallel to detergent action. However, the analogy is superficial and the substantivity of a dye molecule is not increased, for instance, by the mere introduction of a fatty acid chain in order to give it the character of a soap. Surface-active compounds are normally constituted with a head and a tail, of which one is hydrophobic and the other is hydrophilic; the molecules are then adsorbed from aqueous solution on the surface of a substrate, such as the

[71] Standing *et al.*, *Trans. Faraday Soc.* **41,** 506 (1945).

[72] Fishwick and Neale, *Trans. Faraday Soc.* **43,** 332 (1947).

[73] Graham and Fromm, *Can. J. Research* **25F,** No. 6, 303 (1947).

[74] Cf. Venkataraman, *Current Sci.* **8,** 281 (1939).

[75] For measurements of the substantivity of textile assistants, see Mecheels, *Melliand Textilber.* **18,** 103, 165, 312 (1937).

[76] Cf. Rideal in Wetting and Detergency, Harvey, London, 1937.

oily film of a textile fiber, with the long axis more or less perpendicular to the surface with the hydrophilic or ionic end of the molecule in the water phase. Elongated dye molecules, on the other hand, are adsorbed with their axis lying parallel to the cellulose chain; and in contrast with the unsymmetrical distribution of the polarites in surface-active compounds, substantivity in the benzidine type of dye molecule is favored by a structure in which the auxochromes and the ionizing groups are symmetrically distributed over the length of the molecule in such a manner that the polarities are at right angles to the long axis of the molecule.[77]

The water-soluble complexes obtained by heating *p*-phenylenediamine or benzidine with octadecyl bromide (6 moles) in pyridine solution have considerable affinity for cotton.[78] *N,N*-Bisoctadecylsulfanilic acid is substantive to cotton, but not to wool, while stearoylsulfanilic acid has more affinity for wool than for cotton. In general, basic compounds of this type have more affinity for cotton, and acidic compounds more for wool.[78] Fixanol (ICI), which is of the type cetylpyridinium chloride, behaves towards cellulose in the same manner as a rapidly diffusing dye.[79, 79a] The paraffin chains influence the substantivity of these cation-active colloidal electrolytes, since the ordinary basic dyes in which the color is in the cation have little or no affinity for cotton and have to be used on a tannin mordant. When long chain fatty acids are condensed with polyethylene-polyamines, the complex amides form alkali salts which are soluble in water at the boil and are substantive to cotton; such products are useful as softening agents for dyed cotton and rayon and have the advantage over the usual cationic softeners that they do not decrease the light fastness of the dyes.[80] Reference has been made elsewhere to wool dyes containing heavy alkyl groups which have high fastness to severe wet treatments. The affinity for wool of a dye containing an alkyl group appears to increase with increasing chain length of the alkyl group; such an effect has been noticed with alkylsulfonic acids.[144]

Constitution of Dyes Substantive to Cellulose

The affinity of dye for fiber plays an important part in the direct dyeing of cellulose; unlike the acid dyeing of protein fibers, the electrical forces are opposed to the absorption of the dye. While the absorption of a dye from aqueous solution by a fiber is a partition of the dye between the fiber phase and the water phase, resulting in a reversible equilibrium, it is important to remember that practical dyeing depends on the more or less complete transference of the dye to the fiber, i.e., the exhaustion of the dyebath, under suitable conditions. As stated earlier, the dyeing process is exothermic. It is clear from these and other considerations that there is an intermolecular attraction between dye and fiber.

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[77] Cf. Schirm, *J. prakt. Chem.* **144**(ii), 69 (1935).

[78] Seidel and Engelfried, *Ber.* **69,** 2567 (1936).

[79] Whittaker, quoted by Boulton and Morton in Ref. 38. For figures of absorption of Fixanol by cotton, wool, and other fibers, see Blow, *J. Soc. Chem. Ind.* **57,** 118 (1938).

[79a] Because of the negative *zeta* potential of cellulose in water, cotton does not absorb anionic or nonionic surface-active agents from aqueous solution, but absorbs cationic agents; Harris, *Textile Research J.* **18,** 669 (1948).

[80] McLeod, *Am. Dyestuff Reptr.* **37,** 30 (1948); see also Chapters XVII and XL.

The general mechanism of the dyeing process which emerges from the preceding account provides some indications of the structural characteristics of dye molecules which are favorable to substantivity. Direct dyes are electrolytes which are usually colloidal under certain conditions. For a dye to be positively adsorbed from aqueous solution, it must have greater attraction for the cellulose phase than for the water phase, and a tendency to aggregate in aqueous solution is a related property. Expressed somewhat differently, dye molecules or ions aggregate to form colloidal micelles because of their hydrophobic character, as a result of which they displace the water molecules in the intercrystalline regions of cellulose and attach themselves to the cellulose molecules. Since hydrogen-bond formation between the dye and cellulose is the most likely mode of combination, the dye molecule must contain groups, such as azo, amino, hydroxyl, and amide groups, which can fulfil this purpose. It may be assumed that the larger the number of sites in a dye molecule offering points of attachment to the cellulose chain, the greater will be the stability of the combination between dye and cellulose. At least two types of substantive dye molecules may be visualized: an elongated molecule such as a benzidine dye, which orientates itself parallel to a cellulose chain; and a large flat planar molecule which can attach itself to two or more adjacent cellulose chains. Considering that dye absorption occurs in the disordered regions of the fiber, the possibility of nonplanar dye molecules possessing substantivity for cellulose cannot be ruled out (see later). The size of the dye molecule is limited on the one hand by the diameter of the channels in the intercrystalline regions of the cellulose fiber, and on the other by the requirement of a diffusion process in which sorption of the dye on the cellulose substrate can take place and equilibrium attained under practical conditions of dyeing. Thus, Lenher and Smith have compared the substantive Benzopurpurine 4B with its isomeride from *m*-tolidine which is non-substantive under normal dyeing conditions.[81] From diffusion experiments they have calculated the size of the micelles of the two dyes at different temperatures in the presence of varying quantities of electrolytes. At 25° and with low concentrations of electrolyte Benzopurpurin 4B micelles contain several hundred molecules, while the isomer, at the same temperature and in the presence of more electrolyte which increases aggregation, contains less than 20. At this temperature the *m*-isomer is more substantive than Benzopurpurine 4B, but at 80–100° the latter is much more substantive. At 94°, Benzopurpurine is adsorbed ten times as much as the *m*-isomer by cotton and cellophane.[82] The higher temperature causes partial breakdown of the micelles, and at this temperature the size of the 4B particles is reduced to what Lenher and Smith consider to be the maximum size for substantivity, a diameter of 17A.[81] Somewhat similar differences are shown by the dyes Benzo Fast Red 8BL (I) and its benzamido derivative (II). Neither of the dyes has any substantivity in the absence of electrolytes; in their presence (I) is more substantive at 25°, but at the boil is not adsorbed at all, while at this temperature (II) is a fairly substantive cotton dye.[83] "Substantivity" under practical dyeing conditions thus depends not merely on the constitution of the dye, but also on the maintenance of the optimum conditions of temperature and salt concentration. The difficulties in the way of a quantitative assessment of substantivity will be clear from the earlier discussion of dyeing theories, and the following correlations between the chemical constitution of dyes and their substantivity to cellulose are therefore empirical and qualitative.[2]

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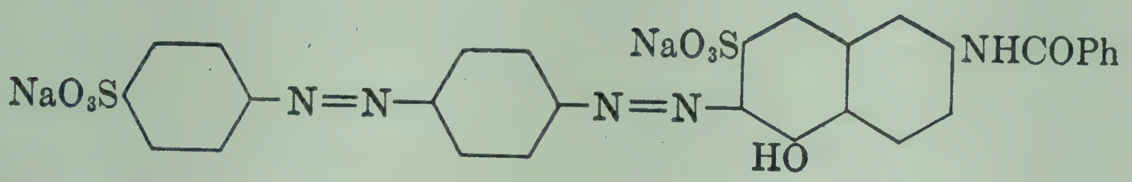
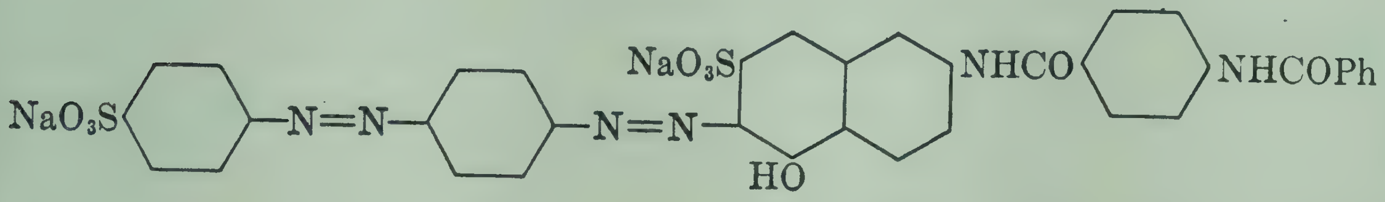
[81] *JACS* **57,** 504 (1935).



(I)

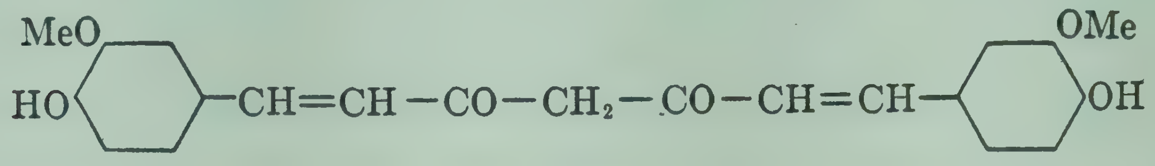


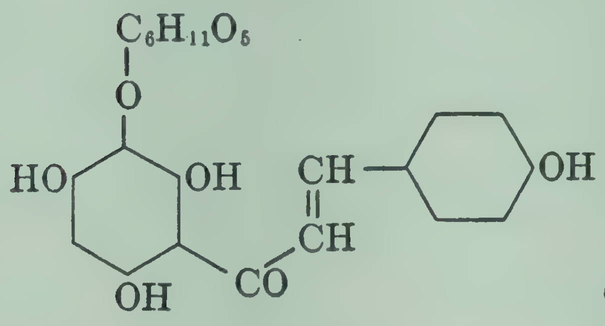
(II)

There are several natural coloring matters (e.g. bixin, carthamin, curcumin, catechin), which do not contain nitrogen or sulfur, and which are substantive to cellulose. Kostanecki (1918) drew an analogy between the elongated symmetrical character of the curcumin molecule and the structure of the benzidine dyes. Carthamin is the glucoside of a chalkone derivative and contains a number of phenolic and alcoholic hydroxyl groups, while catechin is a benzo-γ-pyran derivative containing one alcoholic and four phenolic hydroxyl groups.[84] The synthetic direct

[82] Griffiths and Neale, *Trans. Faraday Soc.* **30,** 395 (1934).
[83] Lenher and Smith, *JACS* **57,** 497 (1935).
[84] See ref. 1, Chapter XXIV.

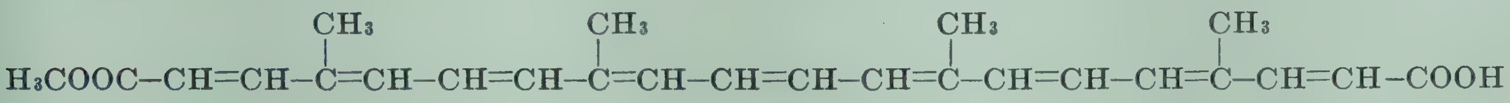
cotton colors belong to a very different type, being sodium salts of aromatic sulfonic acids, which are strong electrolytes and are absorbed as ions, but are present in the dyed fiber as the neutral sulfonates. Marked substantivity to cotton is also shown in alkaline solution by the leuco compounds of many sulfur dyes and anthraquinonoid vat dyes, including some not containing nitrogen and sulfur, and by the arylamides of hydroxynaphthoic acid. Flat polycyclic molecules such as the phthalocyanines and the dibenzanthrones, to which the requisite solubility has been imparted by the introduction of sulfonic groups, have pronounced affinity for cellulose. While the color is in the anion in these dyes, cellulose is also capable of absorbing colored cations if the dye is suitably constituted; thus there are basic azo dyes and phthalocyanines containing ammonium or sulfonium groups which are substantive to cellulose. Color is not an essential property of a substantive molecule, and colorless substances such as polyamides are positively adsorbed by cellulose, although many of the constitutional requirements for color are favorable to substantivity. Thus, substantivity for cellulose is to be found among widely different types of organic compounds. These examples illustrate the variety of structural factors to which substantivity may be due and the improbability of over-simplified explanations standing the test of accumulated experimental data. A closer analysis of the structural features of dyes possessing substantivity may now be attempted.


Curcumin


Carthamin

Conjugated unsaturation. In an important contribution to the theory of substantivity, Schirm[77] suggested that substantivity is associated "with a polynuclear system of conjugated double bonds, the residual valency of which, in conjugation with the auxochromes present, is responsible for the substantivity; groups which interfere with the system of double bonds weaken, and may destroy, the substantivity." However, his conclusions regarding the minimum chain length of eight conjugated double bonds, and the specific arrangements of the conjugated system which he postulated in certain dyes, have no significance in the light of modern structural theory. Increase in substantivity with an increase in the length of a conjugated chain of double bonds is to be anticipated in view of the electron cloud of the conjugated chain and the electronic dispersion forces. Further, the longer the chain the larger is the polarizability and the possibility of interaction with the permanent dipoles of the hydroxyl groups of the cellulose molecule.

Bixin, the coloring matter of annatto, is a remarkable instance of an aliphatic compound which, by virtue of a series of nine conjugated double bonds terminating at one end with a carboxyl and at the other with an ester group, is both colored and substantive to cotton.

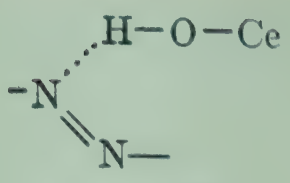


$$H_3COOC{-}CH{=}CH{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH{=}CH{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH{=}CH{-}CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH{-}CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH{-}COOH$$

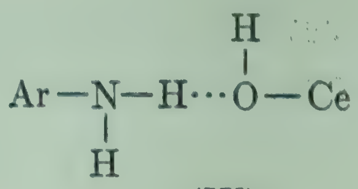
Bixin

Azo dyes. The technically valuable direct cotton dyes belong mainly to the azo class, and the substantivity, like the color, can be largely predicted from the constitution of the dye. The number and types of the aromatic nuclei, the number and positions of the azo groups, and the positions of the amino and/or hydroxyl groups determine the number and types of resonance structures, and in consequence the color of the dye (see Chapter VIII). If in addition we take into account the number and positions of the sulfonic groups, the substantivity of the dye can be broadly gauged. Ruggli[3] and Schirm[77] have reviewed the structural features of azo dyes which are favorable to substantivity towards cotton, and they have also carried out extensive synthetical experiments in this connection.

The azo group is a powerful aid to substantivity and it can apparently function in several ways in the attachment of an organic molecule to cellulose. Substantive azo dyes may be assumed to have the *trans* configuration, although all azo dyes may not be *trans* in configuration and the variations in substantivity from dye to dye may in part be related to configurational differences. By the introduction of two or more azo groups in 1,4-positions we have elongated molecules, which can align themselves with their long axis parallel to the long axis of the cellulose chain, and which are attracted to cellulose by dipole-dipole and van der Waals forces. Hydrogen bonding can occur between the cellulose hydroxyls and the azo groups, or between the cellulose hydroxyls and amino or hydroxyl groups in the dye, as suggested by various workers and shown in (III), (IV), (V) and (VI). Direct cotton dyes

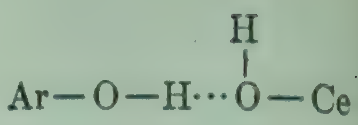


(III)



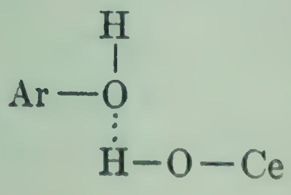
$\mathrm{Ar{-}\underset{\underset{\textstyle H}{|}}{N}{-}H\cdots\overset{\overset{\textstyle H}{|}}{O}{-}Ce}$

(IV)



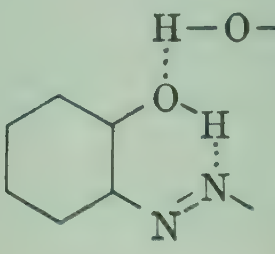
$\mathrm{Ar{-}O{-}H\cdots\overset{\overset{\textstyle H}{|}}{O}{-}Ce}$

(V)



$\mathrm{Ar{-}\underset{\underset{\textstyle H{-}O{-}Ce}{\vdots}}{\overset{\overset{\textstyle H}{|}}{O}}}$

(VI)



(VII)

are mostly *o*-hydroxy or *o*-aminoazo compounds, in which chelation assists the planarity of the molecule and its adherence to the cellulose chain; further, the formation of a chelate hydrogen bond between the azo and *o*-hydroxyl or *o*-amino groups facilitates the formation of a hydrogen bond between the oxygen or nitrogen atom of the hydroxyl or amino groups in the dye and a hydroxyl group in the cellulose molecule, as shown in (VII).

A single azo group is inadequate for the production of the substantivity necessary for practical dyeing, unless other groups favorable to substantivity are also present. Nearly all the azo direct cotton dyes contain two or more azo groups; and the few substantive monoazo dyes owe their substantivity to specific constitutional factors such as thiazole rings or amide groups. Thus the dyes obtained by coupling diazotized dehydrothiotoluidine (one thiazole ring), Primuline (two thiazole rings) and Primuline K (three thiazole rings) respectively with H-acid possess approximately the same substantivity for cotton in spite of their different molecular weights,[85] although it is sometimes suggested that substantivity increases with molecular weight. Ruggli[86] prepared a series of "homologous azo dyes" by coupling the necessary number of molecules of J-acid by the scheme [J-acid → $(\text{J-acid})_n$ → J-acid]. The products, represented by J, 2J, 3J, 4J and 5J, had molecular weights ranging from 260 to 1349, but as each component contained a sulfonic group, the solubility was not affected. The disazo dye was more substantive than the monoazo dye, but further increase in the molecular weight was not advantageous.

Dyes prepared by tetrazotizing benzidine and its derivatives and coupling them with two molecules of the same or different coupling components are well known for their substantivity. Tables IV and V reproduce the experimental results of Griffiths and Neale on the relation between constitution and substantivity in a series of benzidine dyes.[82]

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[85] Levi, *Giorn. chim. ind. appl.* **4,** 62 (1921).

[86] Ruggli *et al.*, *Helv. Chim. Acta* **14,** 127 (1931); **16,** 858, 873 (1933).

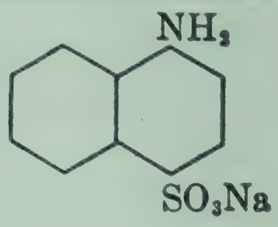
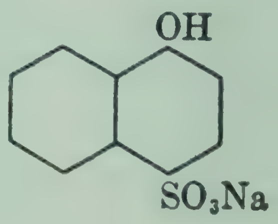
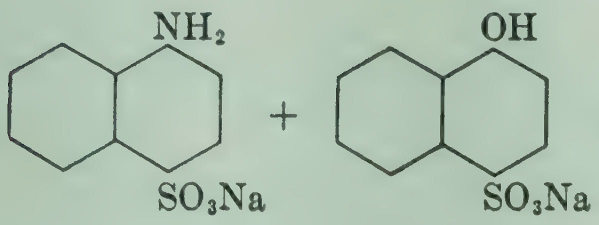
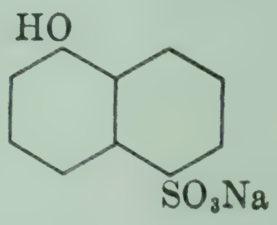
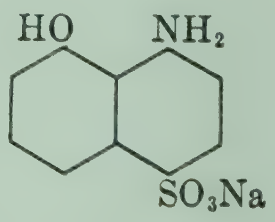
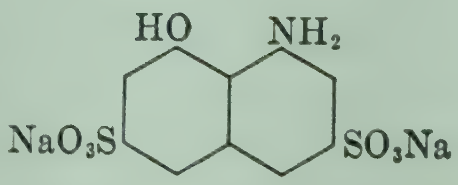
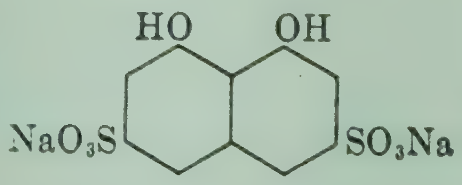
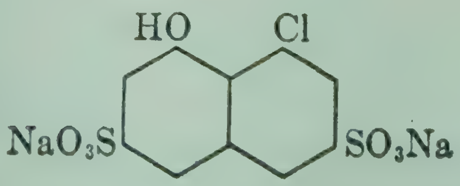
The absorption values are expressed as g. of dye taken up at equilibrium by 100 g. of dry cellulose, using dye liquors consisting of 0.05 g. of the pure dye and 5.0 g. sodium chloride per liter and maintaining the temperature at 90°. The apparent diffusion coefficients[61] are given in cm.^{2} per minute. The dyes in Table I are prepared from benzidine and four of its derivatives, the coupling component being naphthionic acid. The results therefore indicate the effect of substitution in the benzidine nucleus on the substantivity of the disazo dyes. Except for the dye from *m*-tolidine in which the effect of substitution in the 2,2′-positions is a marked lowering of substantivity, the absorption is of the same order; alkyl substitution in the parent diamine increases the substantivity while chlorine and methoxyl have the opposite effect. The dyes in Table V are prepared by tetrazotizing and coupling the same diamine, *o*-dianisidine, with two moles of varied end components; for Azo Violet one mole each of two different end components is employed, and the dye is therefore a structural cross between Benzopurpurine 10B and Benzoazurine G. The replacement of one and two amino groups by hydroxyl, which has an increasingly bathochromic effect, progressively lowers the substantivity. This is consistent with the view that the degree of substantivity is a function of the strength of the hydrogen bonding, which in turn will be determined by the availability of unshared electrons for the purpose. The observed effects are in line with the fact that ammonium compounds are more stable than oxonium compounds. The behavior of Benzopurpurine towards acids (red → blue) and of Benzoazurine G towards alkali (blue → red) is of interest in this connection.

TABLE IV
Substantivity of the Disazo Dyes $D \rightrightarrows (\text{Naphthionic Acid})_2$

		Absorption		*Apparent diff. coeff.*	*Absorption Ratio:*
Dye	*Diamine*	*By viscose*	*By cotton*	$\times 10^{-8}$	*Viscose/Cotton*
Congo Red	Benzidine	3.1	1.2	5.16	2.6
Benzopurpurine 4B	*o*-Tolidine	3.3	1.13	4.6	2.9
Benzopurpurine 10B	*o*-Dianisidine	2.45	0.87	5.18	2.82
Dianol Red 2B	*o*-Dichlorobenzidine	2.84	1.06	3.12	2.68
Isomer of Benzopurpurine 4B	*m*-Tolidine	0.275	0.148	84.0	1.85

The favorable effect of the halogen atom on substantivity is seen

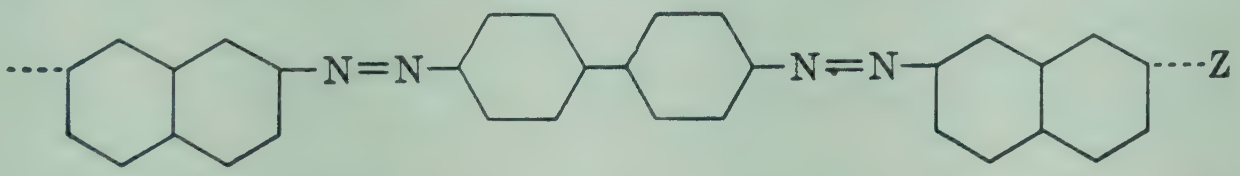
TABLE V
Dyes Prepared from *o*-Dianisidine

Dye	*End component*	*Absorption*		*Apparent diff. coeff.* $\times 10^{-8}$	*Absorption Ratio:* $\frac{\text{Viscose}}{\text{Cotton}}$
		By viscose	*By cotton*		
Benzopurpurine 10B		2.45	0.87	5.18	2.82
Benzoazurine G		1.45	0.70	2.74	2.06
Azo Violet	 NH₂ SO₃Na + OH SO₃Na	2.25	0.923	4.40	2.44
Diamine Blue AZ		2.10	1.24	2.52	1.69
Chicago Blue B	 HO NH₂ SO₃Na	3.40	1.20	1.95	2.84
Benzo Sky Blue	 HO NH₂ NaO₃S SO₃Na	0.945	0.296	10.4	3.2
Dianil Blue G	 HO OH NaO₃S SO₃Na	0.545	0.256	15.1	2.16
Brilliant Azurine B	 HO Cl NaO₃S SO₃Na	0.990	0.388	6.8	2.56

from the absorption data for Brilliant Azurine B; and it has been observed in other groups of dyes, the leuco compound of tetrabromoindigo for instance being much more substantive than leuco indigo. The influence of the sulfonic groups, as evident from Table II, is discussed later.

The introduction of an additional amino group in the end component (cf. Diamine Blue AZ and Chicago Blue B) has no effect on the substantivity to cotton, but it leads to a large increase in the substantivity to viscose, because of the acidic character of viscose in comparison with native cellulose, owing to some oxycellulose formation and higher carboxyl content.

The specific viscosity of methylcellulose in aqueous solution is increased by the addition of substantive dyes of the Congo Red type, apparently because of the formation of methylcellulose-dye complexes.[87] The dyes which are most effective in increasing the specific viscosity are those which have the amino groups on one side and the hydrophilic groups on the other side of the Z plane of the molecule as in Congo Red and Benzopurpurine 4B. The activity is reduced as the number of hydroxyl and sulfonic groups is increased. Valko has stated that the distribution of dipole character over the whole length of the dye molecule and at right angles to it is favorable to substantivity. An examination of the direct cotton dyes of the azo class and of the anthraquinonoid vat dyes reveals that a factor favorable to substantivity is molecular symmetry. Thus Congo Corinth and Congo Red are more substantive than the less symmetrical Congo Rubine.[3]



When dyes containing an asymmetric carbon atom are applied to wool, silk or cotton, there is no difference in the absorption rates of the optically active forms and there is no resolution of the racemic compound.[88] Brode and Brooks[89] prepared optically active and racemic dyes, possessing molecular rather than atomic asymmetry, by tetrazotizing the active and racemic forms of 2,2′-diamino-1,1′-dinaphthyl and coupling with phenyl-J-acid; dye-trials showed that there is no selective absorption of the dyes. Earlier work had led to the conclusion that the active isomers of optically active dyes have the same physical properties, including adsorption by inert and active materials, absorption spectra and fastness to light.

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[87] Centola, *Ricerca sci.* **11,** 905 (1940).

[88] Adams and Brode, *JACS* **48,** 2193 (1926).

[89] *Ibid.* **63,** 923 (1941).

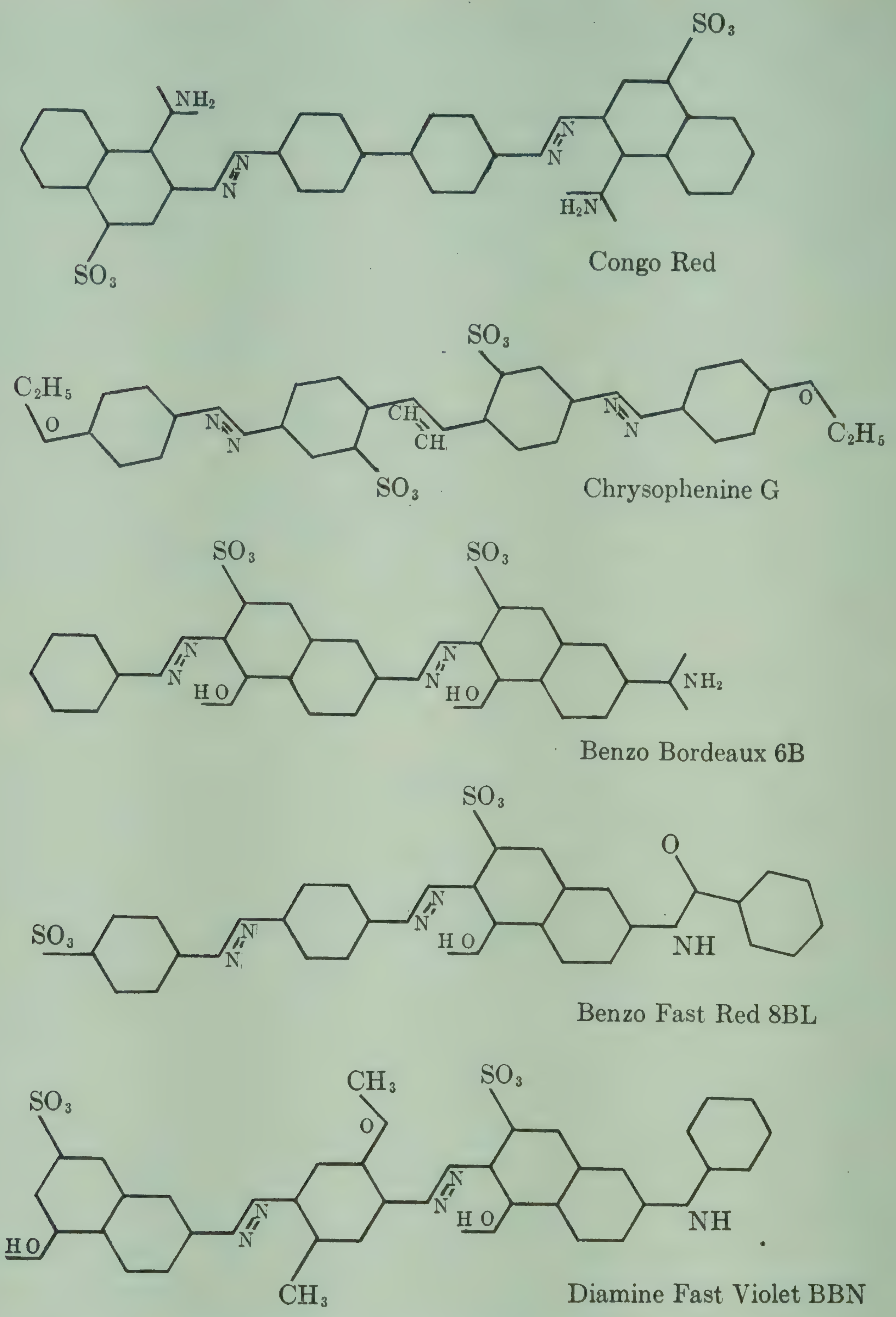
Congo Red
Chrysophenine G
Benzo Bordeaux 6B
Benzo Fast Red 8BL
Diamine Fast Violet BBN

Fig. 7. Scale drawings of the molecules of some direct dyes.

The substantivity of benzidine dyes has been ascribed to their existence in approximately straight-line threadlike form capable of attachment to the straight chains of the cellulose molecules; and there is a similarity in form in the space models of benzidine and allied groups of dyes and those of cellulose and cellobiose.[90] The scale drawings of the molecules of five substantive disazo dyes of different types in Fig. 7 illustrate their flat elongated character and their very rough similarity to the cellobiose units in the cellulose chain-molecule. However, an inspection of the scale drawing (Fig. 8) of Chlorantine Fast Green BLL, a dye which is derived from cyanuric acid and has excellent substantivity for cellulose, clearly shows that a substantive dye molecule need not be elongated or threadlike in the sense of the benzidine dyes. More examples are cited later, and it is necessary to emphasize the point that all substantive dyes are not "long, linear, and planar dye molecules" as stated so frequently.[17, 1a] The essential requirement, so far as azo dyes are concerned, appears to be that the groups capable of hydrogen-bonding are so disposed that attachment with the hydroxyl groups of the repeating cellobiose units in the cellulose molecule becomes possible. A minimum of two hydrogen bonds is apparently necessary for a relatively stable union of dye and cellulose, and the hydrogen-bonding groups in the dye molecule may be spaced at about 10–11A to conform to the repeating units in cellulose; but as seen from the drawings of the five dye molecules in Fig. 7, considerable flexibility in this regard is permissible because of the large number of hydroxyl groups in cellulose. An observation of interest from the point of view of the size and shape of dye molecules and their substantivity for cellulose is that, when cotton is dyed with a mixture of Diphenyl Fast Red 5BL Supra I (Geigy) and Chlorantine Fast Green BLL and then soaped, the immature fibers remain preferentially dyed green and the mature fibers pink.[90a] The difference is apparently

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[90] Meyer and Mark, Der Aufbau der hochpolymeren organischen Naturstoffe, Akademische Verlagsgesellschaft, Leipzig, 1930.

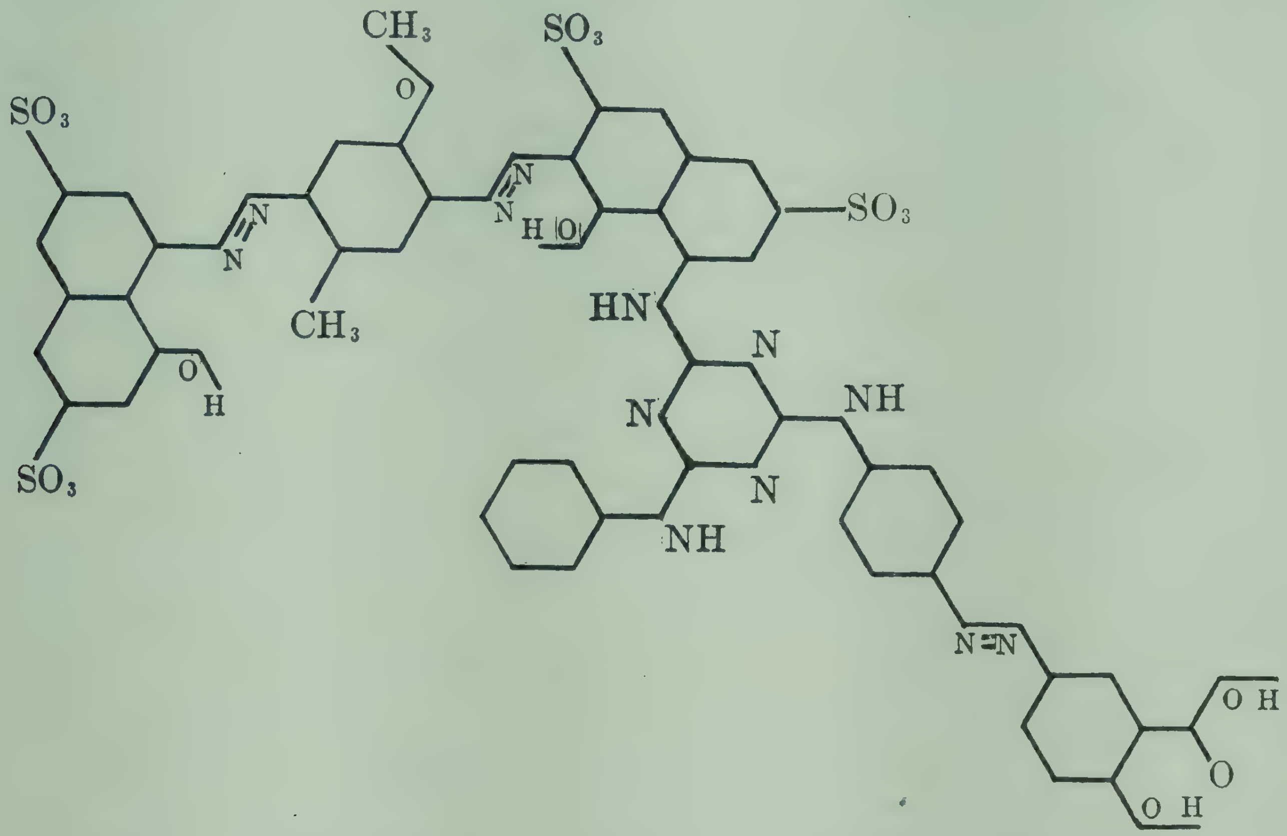
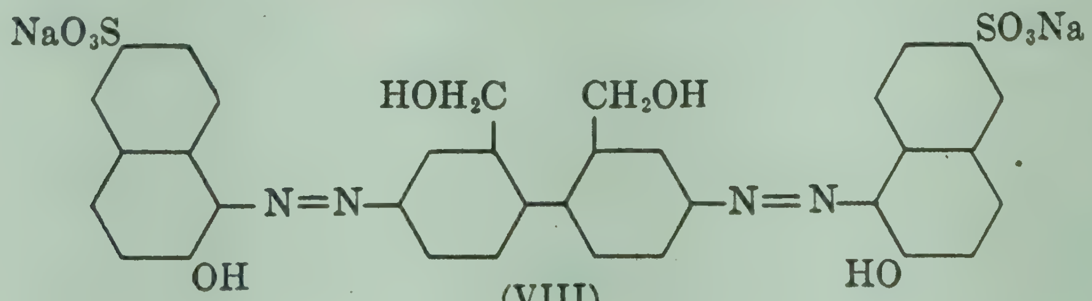


Fig. 8. Scale drawing of Chlorantine Fast Green BLL molecule.

[90a] Goldthwait *et al.*, *Textile World* **97**, 105 (1947).

associated with the larger size and less linear shape of the green dye and the greater availability of space in the less oriented immature fibers.[90b]

The substantivity of benzidine dyes is destroyed or considerably diminished if there are *m*-substituents, but the substantivity is restored if the *m*-substituents form a ring as in 3,6-diaminocarbazole or benzidine sulfone. Reference has been made earlier to the difference between Benzopurpurine 4B and its analog from *m*-tolidine in their aggregation in aqueous solution at different temperatures. Hodgson[91] has suggested that the disappearance of substantivity is due to the non-coplanar character of the 2,2′-substituted diphenyls; and he has postulated a coplanar configuration of the aromatic nuclei as a necessary condition for the production of substantivity in a dye molecule. The coplanarity hypothesis finds support in the nonsubstantivity of dyes from 4,4′-diamino dibenzyl and diaminodiphenylmethane in contrast with the substantive dyes from diaminostilbene and diaminoazobenzene. The necessity for planarity in a dye molecule for attachment to the cellulose chain is, however, by no means clear and we are not yet in a position to define the nature and extent of the relationship between the planarity of dye molecules and their affinity for cellulose; there is no theoretical difficulty in picturing the attachment of large molecules, which are not completely coplanar, to cellulose chains in the amorphous regions of the fiber. Anyhow, some of the available data on the substantivity of dyes cannot be reconciled with any simple statement connecting planarity and substantivity. Disazo dyes from 4,4′-diaminodiphenylsulfide are wool dyes, which are unsubstantive to cotton, but with a slight adjustment in the C—S bond angles, these dye molecules can be planar. There are on the other hand several recorded instances of non-planar dyes with substantivity for cotton. Sen and Sadasivam[92] have noticed that the dye (VIII)



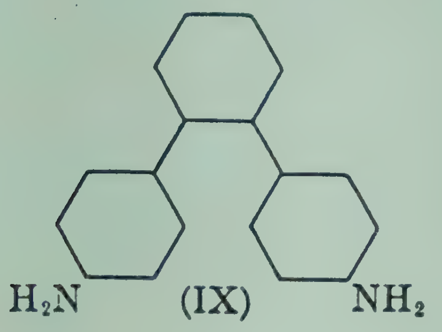
(VIII)

from tetrazotized 2,2′-bishydroxymethylbenzidine and 2-naphthol-6-sulfonic acid is substantive. The significant factor in this dye is probably the hydroxyl in each of the groups in the 2,2′-positions; the hydroxyls might anchor themselves by hydrogen bonding to the alcoholic groups in suitably situated cellulose chains in the disordered regions of the fiber, so that a complicated molecular network between dye and cellulose develops. The second example is a new class of substantive azo dyes described by Allen and Pingert,[93] which are derived from 4,4′-diamino-*o*-terphenyl (IX) and which bear a structural resemblance to the disazo dyes from 4,4′-diamino-*cis*-stilbene (X). A non-planar configuration has been reported for *o*-diphenylbenzene,[94] and the disazo dyes from (IX) cannot be planar. A third anomalous example is the substantivity of the dyes obtained by coupling iodinated diaminodiphenylmethanes with Chicago acid. The dye (XI), in which the benzidine component cannot be planar, is a brownish black dye for cotton.[95] Acid anthraquinone dyes, prepared by the condensation of 4-bromo-1-aminoanthraquinone-2-sulfonic acid (XII) with aromatic amines and normally employed as wool dyes,[96] acquire substantivity for cotton if an azo group or an amide group is present in a suitable position in the amine component. Examples of such amines are (XIII), (XIV) and (XV).

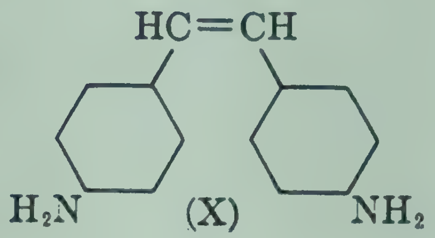
[90b] Work, *Textile Research J.* **19**, 392 (1949).

[91] *J. Soc. Dyers Colourists* **49**, 213 (1933).

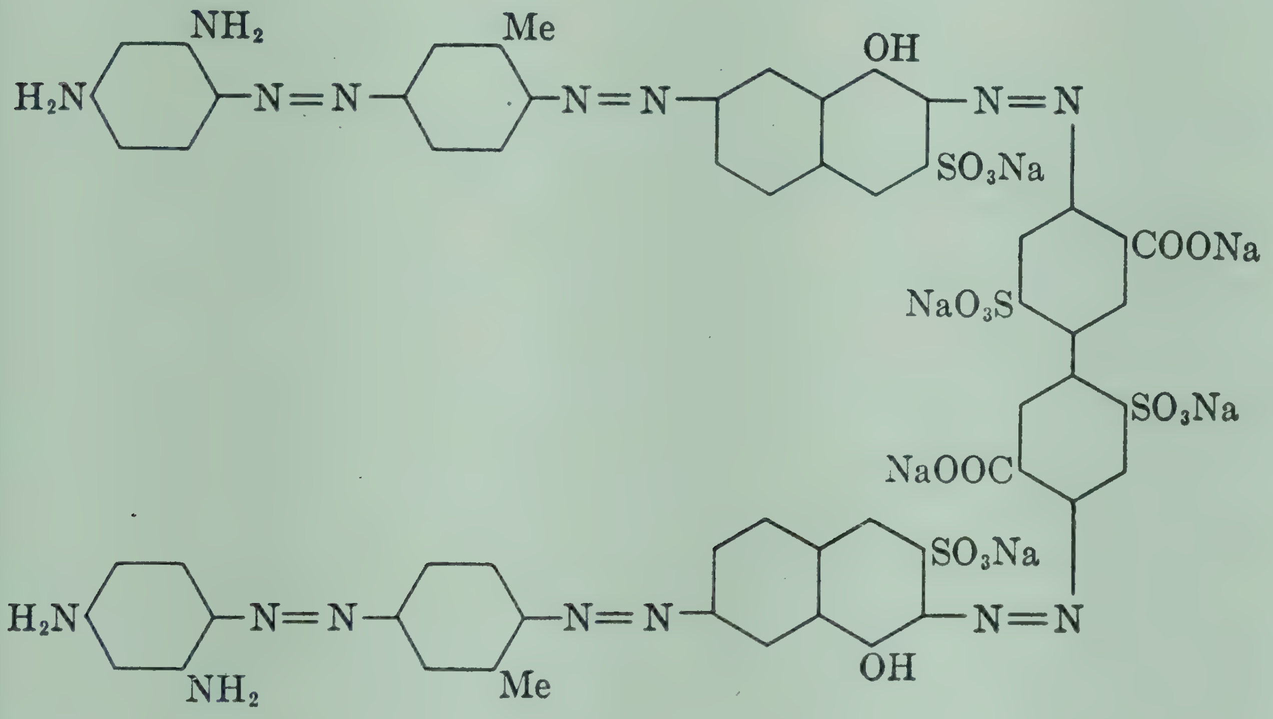
[92] *J. Indian Chem. Soc.* **9**, 403 (1932).



(IX)



(X)



(XI)

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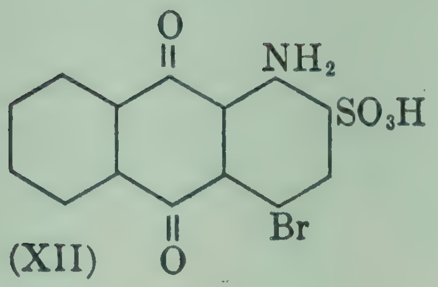
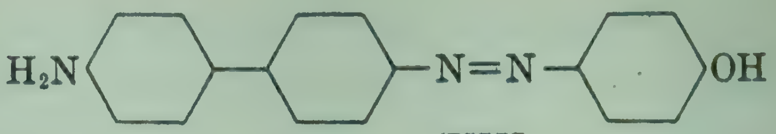
[93] *J. Org. Chem.* **9,** 50 (1944).

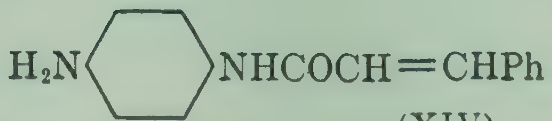
[94] Clews and Lonsdale, *Proc. Roy. Soc. London* **A161,** 493 (1937).

[95] Markush, Miller and Pharma-Chemical Corp., USP 2,164,932.

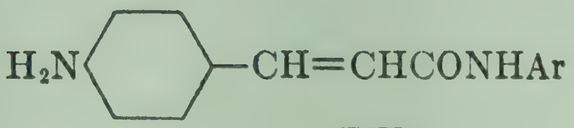
[96] See Chapter XXIX.

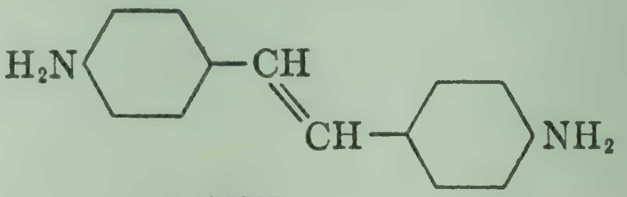

(XII)


(XIII)


(XIV)

In order to test the validity of the hypothesis that for a dyestuff to have substantivity for cotton it must have an elongated linear structure so that it may lie adsorbed along the threadlike cellulose molecule, Ruggli and Lang[97] prepared dyes from the *cis* and *trans* forms of 4,4′-diaminostilbene (X) and (XVI) by tetrazotizing and coupling with naphthionic acid and NW-acid. If a linear configuration were essential, only (XVI) should give substantive dyes. Actually the dyes from (X) were not less substantive than those from (XVI). Reduction of the dyes to the original *cis*- and *trans*-diamines showed that no rearrangement had taken place during coupling. The dyes from the *cis*-diamine gave absorption bands nearer the violet end of the spectrum. The deeper color of the dyes from the *trans*-stilbene is in accordance with expectation; in the *cis* molecule, the *ortho* hydrogen atoms will prevent a planar arrangement of the molecule and inhibit the optically important resonance.


(XV)


(XVI)

It is only for a comparatively small number of compounds that the planarity of the molecule has been investigated by the X-ray diffraction or electron diffraction method. Thus the molecules of oxalic acid, urea (except for the hydrogen atoms), diphenyl, terphenyl, quaterphenyl, diphenylacetylene, *p*-benzoquinone, 1,3,5-trinitrobenzene, naphthalene, anthracene, chrysene, cyanuric triazide and the phthalocyanines have been shown to be planar. It has been calculated from a precise electron diffraction analysis of diphenyl[98] that the separation of the 2- and 2′-hydrogen atoms in a coplanar diphenyl molecule would be 1.84A, and since the nearest approach of hydrogen atoms in different molecules is 2.0A, energy is required to force the diphenyl molecule into coplanarity. Crystals of *trans*-stilbene and *trans*-azobenzene contain two sterically different molecules, half the molecules being planar and half nonplanar.[99] Scale drawings of dye molecules, employing standard bond lengths, bond angles and van der Waals radii of atoms and groups,[99] are useful in judging their planarity. Thus the drawing of the *o*-ditolyl molecule (Fig. 9) indicates the overlapping of the radii of the methyl group and the hydrogen atom in the positions adjacent to the diphenyl linkage, as a result of which the molecule is distorted from planarity. The introduction of methyl groups in the 2,2′- and 6,6′-positions of the benzidine nucleus in benzidine dyes inhibits coplanarity and has a marked effect on the absorption spectra.[100] The steric inhibition of resonance has a hypsochromic effect on color,[101] and color and substantivity thus run parallel to each other so far as the effect of coplanarity is concerned; with the same end components, the diamines which yield substantive disazo dyes also give deeper colored dyes than the diamines which yield unsubstantive dyes.[102] Another consequence of the distortion from planarity is a reduction in the interpenetration of electronic orbitals, resulting in a marked lowering of the intensity of absorption. In attempts to relate substantivity to the planarity of dye molecules, a decrease in the intensity of absorption and a weaker dyeing produced in consequence should not be confused with a decrease in substantivity. Much more extensive and accurate data on the geometry of dye molecules, their light absorption characteristics, and their substantivity as determined by direct measurements of the absorption of the dyes by cellulose, will have to be accumulated before a general theory of substantivity in relation to planarity can be postulated. Brooker has recently made a very interesting study of steric hindrance to planarity in a series of cyanine dyes, and has shown that the absorption maxima can be shifted to longer wave lengths as a result of "crowding" the two nuclei of a cyanine out of a common plane;[103] this results if the effect of the crowding substituent is to lower the stability (or the resonance energy) of the dominant structure. He has also touched on the connection between steric hindrance, planarity and molecular aggregation, and it will be remembered that the tendency of a dye to aggregate in aqueous solution is an indication of its substantivity.

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[97] *Helv. Chim. Acta* **19**, 996 (1936).

[98] Karle and Brockway, *JACS* **66**, 1974 (1944).

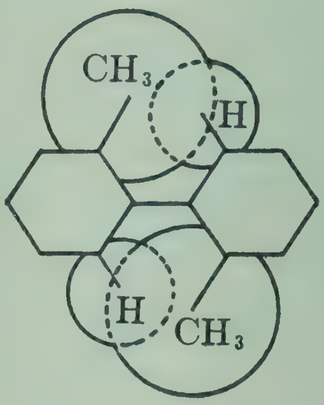

Fig. 9. Scale drawing of *o*-ditolyl molecule.

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[99] See Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca, New York, 1940; see also Wheland, the Theory of Resonance, Wiley, New York, 1944.

[100] Morris and Brode, *JACS* **70,** 2485 (1948).

[101] See Chapter VIII.

[102] See also Blumberger, *Rec. trav. chim.* **63,** 127 (1944).

[103] Brooker *et al., Chem. Revs.* **41,** 325 (1947); see also Brunings and Corwin, *JACS* **64,** 593 (1942).

J-Acid derivatives. Many azo dyes of which J-acid is a component have good substantivity. The technically important dyes are disazo or trisazo dyes in which J-acid or *N*-benzoyl-J-acid is the end component, or disazo dyes from J-acid urea (carbonyl-J-acid) or di-J-acid. The advantage of using J-acid, in contrast for instance to H-acid or γ-acid, as an alkali-coupled middle component in the preparation of disazo dyes for cellulose is that the structure of the dyes is linear. In a quantitative study of the substantivity of azo dyes derived from J-acid, Ruggli and Leupin[104] have observed that the substantivity of J-acid dyes is not so general as hitherto assumed. Certain substituents, such as an *N*-acyl group, and indeed the whole combination of components, are important. Substantivity and power of diffusion are opposed to one another. The monoazo dyes (A → J-acid) are not substantive, and the value of 15, which Ruggli regards as the threshhold value for substantivity defined by his procedure outlined earlier, is attained by the dye (aniline → *m*-aminobenzoyl-J-acid). Even the disazo dye (aniline → carbonyl-J-acid ← aniline) does not approach the substantivity of Congo Red. The most substantive dye among those examined by Ruggli was the disazo dye (dehydrothiotoluidine → J-acid → J-acid), which is not used technically. In the commercially valuable J-acid dyes, *p*-aminoacetanilide is one of the frequently used diazonium components.

Amide groups. Carboxyamide (—CO—NH—) groups are favorable to substantivity as illustrated by the increased substantivity of dyes from *N*-benzoyl-J-acid and the urea from J-acid. The amide group is an important feature of the arylides of hydroxynaphthoic acid and the acylamidoanthraquinones. Enolization to —C(OH)=N— and conjugation with other double bonds in the molecule have been suggested by Schirm as strengthening the auxiliary valency forces at the end of the conjugated chain, leading to increased adsorption of the elongated dye molecule on the cellulose molecule. Schirm relates the substantivity of urea derivatives to "half enolization" of the urea group. There is no justification, however, for assuming such enolization and the available evidence is in fact in favor of the amide, rather than the imido-enol structure. The infrared absorption spectra of a number of simple amides show that they exist predominantly in the ketonic form with extensive association due to hydrogen bonding.[105] Krzikalla and Eistert[106] pictured the union between dyes containing —CO—NH— groups and cellulose as follows:

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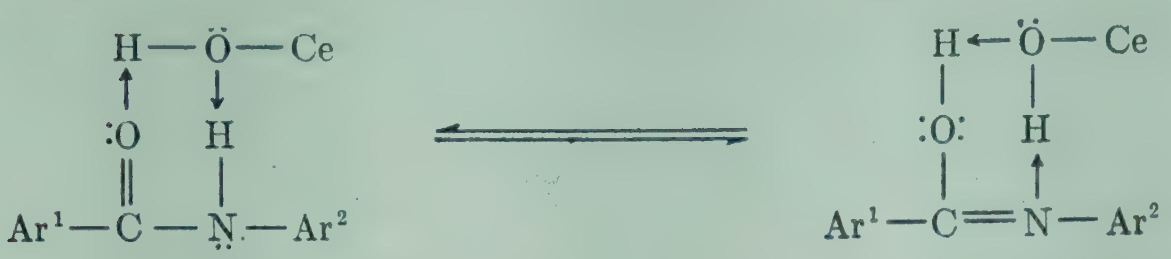
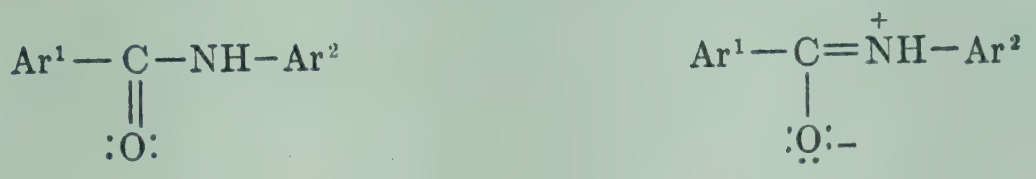
[104] *Helv. Chim. Acta* **22,** 1170 (1939).

[105] Richards and Thompson, *J. Chem. Soc.* 1248 (**1947**).

[106] *J. prakt. Chem.* **143,** 50 (1935); *Ann.* **556,** 91 (1944).



The amide resonance (XVIIA and B), reinforced by resonance interaction with conjugated systems, would appear to favor affinity for cellulose. The tendency of the —CO—NH— group, with its unshared electron pairs,

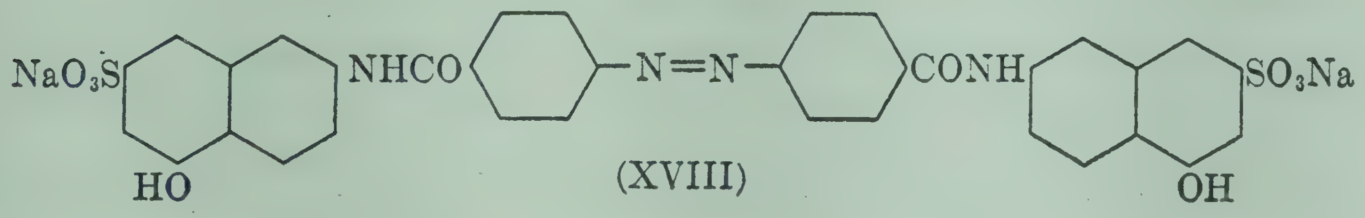


(XVII)

(A) (B)

to impart to a dye molecule the property of ready attachment to cellulose is understandable in view, for instance, of the affinity of amides and anilides for water with which they tend to form complex aggregates.[107] For a clearer understanding of the role of the amide group in the affinity of dyes for cellulose, data on the configuration and dimensions of the amide group will be useful.

Among azo dyes from J-acid, increase in the number of —CO—NH— groups enhances substantivity. The azo dyes from (XVIII) and the corresponding azoxy compound have strong affinity for cotton.[108] A triple amide group can be obtained by interaction of amines with cyanuric chloride, and this reaction has been used for the production of high substantivity (see Chapter XVI).



(XVIII)

Amides derived from α,β-unsaturated acids are especially substantive. Excellent affinity for cotton has been claimed for the monoazo dyes in which the diazonium component is mono-cinnamoyl-*p*-phenylenediamine and the coupling component is an *N*-cinnamoyl-H-acid or -J-acid.[109] Saturation of the double bond destroys the substantivity.

A good example of the influence of the amide group on substantivity is provided by the acylamidoanthraquinones. While anthraquinone and the aminoanthraquinones can be vatted, the alkali salts of the leuco compounds have no affinity for cellulose; but the leuco derivatives of the benzamidoanthraquinones (especially the benzoyl derivatives of 1,4- and 1,5-diaminoanthraquinones) have enough substantivity for practical dyeing, although the substantivity represents about the minimum among the commercial vat dyes for cotton. The dyeing property of the leuco derivatives of anthraquinones carrying acylamido groups in one or more of the α-positions is partly concerned with the resonance of the amide group and its ability to provide points of attachment between dye and cellulose, but there must be other factors, since similar β-compounds have much less substantivity. The absorption spectra of α- and β-benzamidoanthraquinones show that, as in the amines themselves, the α-compound absorbs at longer wave length in the visible region and the intensity of absorption is also slightly greater. The leuco derivative of α-benzamidoanthraquinone in alkaline solution also absorbs in the visible region at longer wave length and more intensely than the β-isomer. Hydrogen bonding between the NH group and the adjacent oxygen atom in the anthraquinone nucleus, which can be postulated only for the α-compound, may be concerned in these differences between α- and β-benzamidoanthraquinones.[110]

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[107] Lassettre, *Chem. Revs.* **20,** 259 (1937).

[108] IG, DRP Anm. I. 35,689.

[109] Deuts. Hydrierwerke, BP Appl. 2195/1933.

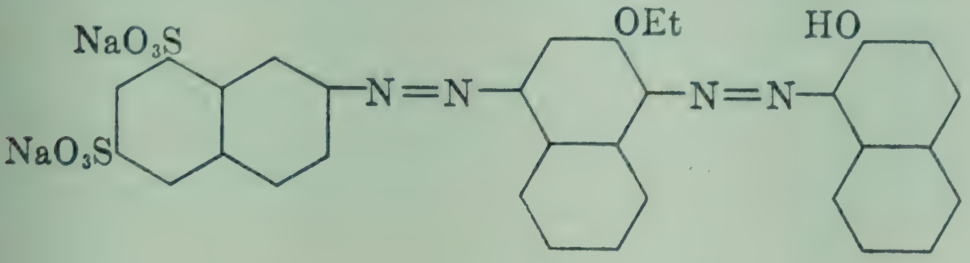
An interesting example of a colorless substance in which substantivity is secured by the multiplication of amide groups is Diazo Light Yellow 2G (see Chapter XII). Colorless stilbene derivatives, such as Blankophor R (see Chapter XX), have affinity for cellulose.

Sulfonic groups. Multiplication of sulfonic groups increases water solubility and leveling power, but usually reduces substantivity. The dyeing properties also depend on the position of the sulfonic groups with respect to the azo groups. The influence of both the number and the position of the sulfonic groups is clear from the results recorded in Table V. All the dyes containing four sulfonic groups exhibit a lower order of absorption than the disulfonic acids. Comparing Benzoazurine G and Diamine Blue AZ, the shift of the sulfonic group in the end component further from the point of attachment of the azo group increases the substantivity considerably. Schirm[77] has suggested that, if sulfonic groups are so situated that the polarity is distributed uniformly along the molecule and perpendicular to its length, substantivity is favored; the dye molecule can then attach itself parallel to the cellulose chain with the hydrophilic sulfonic groups in a perpendicular direction away from the fiber.[110a] The attachment of the Congo Red type of dye to

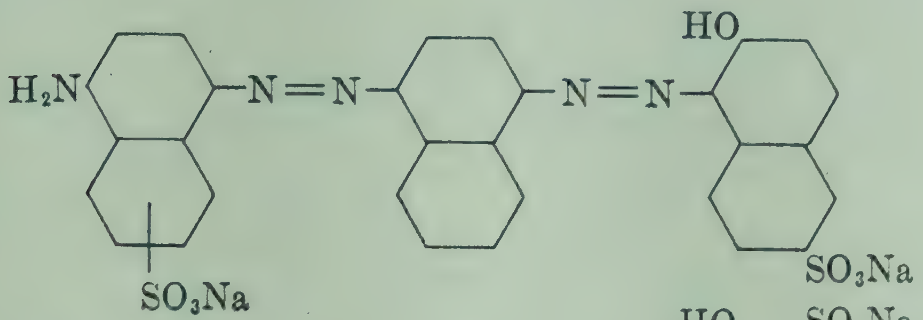
[110] Rao and Sunthankar, unpublished work.

[110a] Vickerstaff in Ref. 1*a* cites the increase in the hygroscopicity of cotton on dyeing with a direct dye as proof for the view that dye molecules lie along the cellulose chain with the plane of the aromatic rings at right angles to the plane of the glucose rings and the solubilizing groups directed towards the aqueous phase.

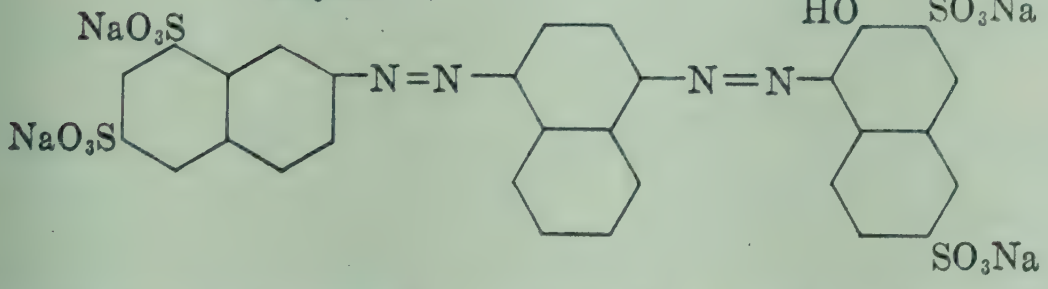
cellulose may thus be regarded as hydrogen bonding between the amino groups of the dye and two primary hydroxyl groups on the same side of two neighboring cellobiose units, the sulfonic groups being disposed away from the cellulose chain. Further examples of the influence of the number and position of the sulfonic groups are Diamine Blue 6G, Diaminogen Blue BB and Naphthol Black B; the first two are direct cotton dyes and the third is an acid dye for wool. Schirm[77] and Hodgson and Marsden[111] relate the differences in the affinity to certain rigid arrangements of single and double bonds in these resonance hybrids; but Naphthol Black B is unsubstantive to cellulose mainly because of the increase in solubility produced by the two additional sulfonic groups. The inferior substantivity of the dyes derived from H-acid as end component in comparison with similar dyes from J-acid and γ-acid is to be similarly ascribed in part to the greater solubility of the H-acid dyes. Sulfonic groups have a powerful tendency to hydrate and dyes containing more than the optimum number of sulfonic groups are attracted more by the water phase than they are by the cellulose phase; it will also be remembered that the *zeta*-potential of cellulose is negative and will repel an anion.[58] The factors enabling Diamine Blue 6G and Diaminogen Blue BB to be used as direct cotton dyes are the 1,4-disazo group, the *o*-hydroxyazo group and the three naphthalene rings, combined with the presence of only two sulfonic groups; the primary amino group in Diaminogen Blue BB and the ethoxyl group in Diamine Blue 6G are also favorable factors.



Diamine Blue 6G



Diaminogen Blue BB



Naphthol Black B

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[111] *J. Soc. Dyers Colourists* **60,** 210 (1944).

The azo group is potent for substantivity, and the mere multiplication of azo groups in 1,4-positions is adequate for the production of technically valuable direct cotton dyes, if the solubility is controlled within desirable limits by the introduction of sulfonic groups in suitable positions. Thus there are disazo, trisazo and tetrakisazo dyes in the commercial range (e.g., Brilliant Benzo Green B, Naphthogen Blue 2R and dyes mentioned in Chapter XV) which are prepared by the scheme ($A \rightarrow M^1 \rightarrow M^2 \rightarrow E$) and which do not employ specific intermediates for substantive dyes, such as benzidine and J-acid.

Sulfur atoms. According to Ruggli,[3] sulfur atoms in any form lead to substantivity, but a restriction to ring systems containing sulfur would be more justified. Thus the disazo dyes from 4,4′-diaminodiphenyl sulfide are not direct cotton dyes, but acid dyes for wool. Primuline, Naphtol AS—L4G and some of the sulfurized anthraquinonoid vat colors containing thiazole rings, and the greater substantivity of leucothioindigo in comparison with leucoindigo, are relevant examples. Leuco compounds of sulfur dyes are substantive, and in the few sulfur dyes of which the constitution has been determined, part of the sulfur is in the form of thiazole or thiazine rings. Thiophenolic groups produced by reduction of disulfide bridges with sodium sulfide contribute to the substantive effect.

Substantivity is aided not only by sulfur-containing rings, but also by the pyrazolone and other heterocyclic systems. The substantivity of compounds of the Naphtol AS and Naphtol AS—G type, for instance, may be increased by the introduction of heterocyclic rings, and various examples have been cited in Chapter XXII.

Condensed polynuclear systems. Among dyes of a given type the substantivity increases from the benzene to the naphthalene, anthracene and the more complex polynuclear aromatic systems. The leuco compounds of many of the anthraquinonoid vat colors in alkaline solution are characterized by good substantivity to cellulose. The leuco compounds, for instance, of dibenzanthrone, its 16,17-dimethoxy derivative and isodibenzanthrone are highly substantive. It will be remembered that both the wave length and the intensity of maximum absorption increase in the order benzene, naphthalene, anthracene, etc.; and it is probable that the resonance of the molecules with which the absorption characteristics are associated[101] is also involved in the substantivity of the dyes derived from these ring systems. Large flat molecules in solution have a tendency to polymerize face to face owing to an electronic resonance between the molecules, as indicated sometimes by the development of a *z* band in the absorption spectra;[101] and aromatic hydrocarbons are increasingly able to form addition compounds (e.g. with picric acid) as the size of the ring system increases. The larger polarizability of the larger ring systems enhances the possibility of interaction between dye and cellulose. Although it has been suggested that the main mechanism by which dye molecules are attached to cellulose is the hydrogen bridge, it is now apparent that, even in the absence of such bonding, the dispersion forces and the electrostatic forces due to the permanent dipoles in the cellulose and dye molecules would be sufficient to account for the intermolecular attraction between cellulose and dyes, such as the leuco derivatives of the anthraquinone vat dyes, containing condensed polynuclear aromatic ring systems. Hydrogen bonds between the cellulose hydroxyls and the oxygen atoms of the quinone groups in the dyes after oxidation of the leuco compounds to the parent anthraquinones are not, however, excluded. The greater the number of benzenoid rings in the condensed ring system, the larger will be the resonance energy, and one effect of resonance will be coplanar configuration of the molecules. The leuco derivative of 16,17-dimethoxydibenzanthrone (Caledon Jade Green) is highly substantive, but we have no data on the planarity of the molecule. The overlapping of the van der Waals radii of the vicinal methoxyl groups is clear from the scale drawing of the molecule in Fig. 10, but because of the great tendency of polynuclear aromatic ring systems to assume a planar configuration owing to the very high energy of resonance stabilization, it is probable that the molecule is forced into planarity by adjustments in the bond angles. Brooker's observation among the cyanine dyes, that by the introduction of groups which distort the dye molecules from planarity the wave length of maximum absorption is increased, has been mentioned.[101, 103] The difference in the light absorption of dibenzanthrone and 16,17-dimethoxydibenzanthrone is a similar example. The steric hindrance due to the 16,17-hydrogen atoms in dibenzanthrone is greatly increased by the methoxyl groups in the same position in Caledon Jade Green, and since the additional energy required for achieving planarity has to be deducted from the resonance energy, the dimethoxy

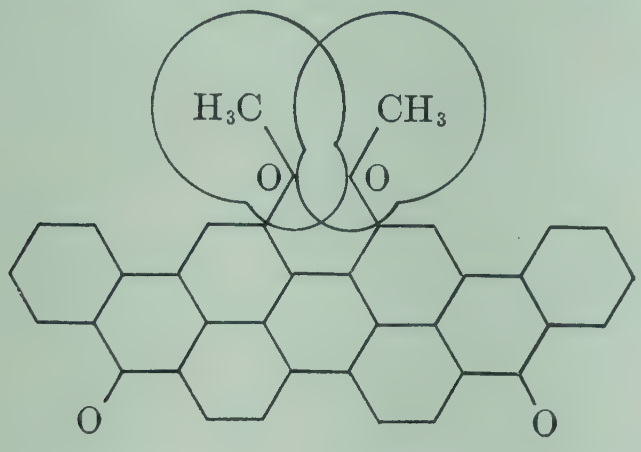


Fig. 10. Scale drawing of Caledon Jade Green molecule.

compound has its maximum absorption at a higher wave length than dibenzanthrone itself; dibenzanthrone dyes blue and the dimethoxy compound bluish green. At the same time, there is a reduction in the intensity of the maximum wave length absorption of the dimethoxy compound.

The older conceptions of substantive dyes as those possessing long thread-like molecules of approximately straight-line form, which were based on the benzidine type of azo dyes, must be modified in view of the constitution of the substantive leuco compounds of the anthraquinone vat dyes. The affinity of a complex polynuclear dye containing a number of quinone groups, such as Indanthrene Khaki GG, probably involves the attachment of the dye molecules to several parallel cellulose units at suitable points, so that the dye molecules act as bridges or grids in a three-dimensional network. A computation from available data indicates the dimensions of the flat Indanthrene Khaki GG molecule (assuming its tetracarbazole structure which is by no means certain) to be slightly over 16A along one axis and over 17A along the perpendicular axis; this dye would appear to represent the limiting size of a molecule, which can migrate into the submicroscopic channels of cellulose fibers. Morton has found that ramie dyed with many vat dyes exhibits little or no dichroism; exceptions are Caledon Yellow 5G, Caledon Gold Orange 3G and Caledon Yellow 2R.[112] In the reduced form the dyeings show positive dichroism.[52] He therefore concluded that the molecules of the substantive leuco compounds are oriented by the cellulose molecules, but not the oxidized dye molecules.[52] However, this cannot be regarded as proof that the dye molecules are retained within the cellulose merely by virtue of their insolubility. Incidentally, a chemical change has been observed in cellulose dyed with vat and azoic dyes in contrast to cellulose dyed with direct cotton dyes; the technique employed is to strip the dye from the fiber by means of pyridine, dissolve the cellulose in cuprammonium hydroxide and examine the optical activity and viscosity of the solution.[113]

Angular configuration of condensed ring systems is a common feature of anthraquinone vat dyes. Among the isomeric dihydroanthraquinoneazines, the product which possesses the substantivity necessary for practical dyeing is indanthrone, having the *bis*-angular orientation. Other examples are the *bis*-acridone, Indanthrene Violet BN, and the carbazoles from the 1,1′-anthrimides. Bradley[114] has drawn an interesting analogy between the relation of the structure of the higher aromatic hydrocarbons

[112] Preston in Ref. 52.

[113] Brass and Schreier, *Kolloid-Z.* **108,** 155 (1944).

[114] *Nature* **137,** 404 (1936).

to their carcinogenic activity and the relation of the structure of an anthraquinone derivative to the affinity of its leuco derivative for textile fibers. Among the hydrocarbons related to anthracene, those derived by attachment of alkyl groups or hydrocarbon rings to the 1,2- or 1,2,5,6-positions possess carcinogenic activity, while other orientations are inert with few exceptions.[115] The same angular orientation of fused rings appears to be equally significant in determining the dyeing properties of anthraquinone derivatives. While 1,2-benzanthraquinone is a feeble vat dye, neither anthraquinone nor naphthacenequinone has affinity. The 1,2-benzopyrene nucleus is equally potent as a carcinogenic structure or as a unit in the structure of vat dyes. 1,2-Benzopyrene itself is a much more powerful carcinogenic agent than 1,2-benzanthracene or 1,2,5,6-dibenzanthracene. Similarly, as vat dyes, 2,3,7,8-dibenzopyrene-1,6-quinone (*trans*) is much more substantive than 1,2-benzanthraquinone, and more than the *cis*-compound (2,3,6,7-dibenzopyrene-1,8-quinone). Although there is no evidence of chemical interaction in carcinogenesis, Fieser has shown that the carcinogenic hydrocarbons have a remarkable tendency to undergo substitution reactions, and a particularly striking instance is the ability to couple with diazonium salts.[116] Wheland and Pauling have correlated the reactivity of aromatic systems with the π-electron distributions in the molecules.[117] Attempts have also been made to correlate the carcinogenic activity of polycyclic aromatic hydrocarbons with an optimum density of π-electrons in certain positions.[118] These considerations are of interest in studying the relation between the structure of anthraquinone vat dyes and the affinity of their leuco compounds for textile fibers.

Carrying out the first quantitative study of the absorption by cotton of vat dyes from alkaline solutions of their leuco compounds, Geake has correlated the effect of pyridine in diminishing the absorption with its effect in raising the redox potential of the system formed by the solution of the leuco dye in equilibrium with the solid oxidized form.[119]

The conversion of leuco vat dyes into the sodium salts of the sulfuric esters (Indigosols and Soledons) greatly reduces the substantivity. The reduction in substantivity may be correlated with the change in the colloidal and electrochemical character of the solution, as well as the restraining influence of the sulfuric ester groups on the resonance of the molecules. Among the Indigosols and Soledons, the anthraquinone

[115] Cook *et al.*, *Proc. Roy. Soc. London* **B111,** 455, 485 (1932); **B117,** 318 (1935).
[116] See p. 838, ref. 395, Chapter III.
[117] *JACS* **57,** 2091 (1935); see also Longuet-Higgins and Coulson, *JCS* 971 (**1949**).
[118] Pullman, *Ann. chim.* **2,** 5 (1947); Pullman and Pullman, *Experientia* **2,** 364 (1946).
[119] *J. Textile Inst.* **40,** T57 (1949)

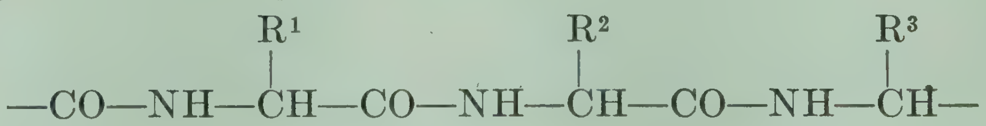
derivatives have in general higher substantivity than the indigo and thioindigo derivatives, and in each group the substantivities run roughly parallel with those of the vats of the parent dyes.

Sulfonic acids of some polycyclic compounds have enough substantivity for cellulose to be used as cotton dyes. Examples are the *bis*-oxazines and fluorindenes mentioned in Chapter XXV. The polycyclic anthraquinonoid vat dyes, such as dibenzanthrone, are substantive not merely in the form of their leuco derivatives, but they also exhibit appreciable cotton affinity when they are sulfonated.[120]

Sulfonated phthalocyanines are substantive to cellulose fibers. While the ammonium, sulfonium and oxonium salts normally used as basic dyes have little or no affinity for cellulose, basic dyes derived from phthalocyanine have been prepared which are substantive to cellulose. Even the tetradiazonium salts from tetraminophthalocyanines possess affinity for cellulose, and this is doubtless associated with the flat planar character and the complete aromaticity of the phthalocyanines (see Chapter XXXVII).

The Affinity of Dyes for Wool

The physical properties of the wool fiber have been described earlier (see Chapter VI). Chemically, wool is a protein belonging to the large group of keratins, characterized by their yielding the sulfur-containing amino-acid cystine as a product of hydrolysis. The nitrogen content of wool keratin is about 17% and the sulfur content is variable within the limits of 2.5 to 4.5%. Wool is in fact much more variable in its composition than the cellulose fibers, not only in different wools, but also in different parts of the same fiber, although the essential chemical character is representative of keratin as a protein type. Acid dyes stain the cortex more heavily than the medulla, and the reverse effect is obtained with basic dyes.[121] While wool and silk are both polypeptides of the general form



$$\text{—CO—NH—}\overset{\overset{R^1}{|}}{\text{CH}}\text{—CO—NH—}\overset{\overset{R^2}{|}}{\text{CH}}\text{—CO—NH—}\overset{\overset{R^3}{|}}{\text{CH}}\text{—}$$

wool has a much more complex chemical constitution since there are wider variations in the side chains R. Silk fibroin is composed mainly of four amino acids, glycine (43.8%), alanine (26.4%), serine (12.6%), and tyrosine (10.6%), which total 93.4 g. per 100 g. fiber; eleven other amino acids make up 19 g.[122] Eighteen amino acids have been identified among the hydrolytic products of wool. Unlike silk, wool contains only about 20% of low molecular weight amino acids, and nearly 50% by weight of wool protein is in the side chains.[123] The amino acids of wool which mainly influence its chemical reactivity and dyeing properties are cystine (12.7%); three acids containing basic side chains—arginine (10.4%), histidine (0.7%), and lysine (3.3%), hydroxylysine being present in minute amount (0.21%); two aminodicarboxylic acids—glutamic acid (15.3%) and aspartic acid (7.3%). Tyrosine (5.8%), serine (9.4%), and threonine (6.76%), which contain hydroxyl groups, may play a minor part in dyeing by hydrogen bonding with azo and other suitable groups. Nearly the whole of the sulfur in wool can be accounted for as cystine; methionine is present only to the extent of 0.71%. The nature of the side chains indicates that the keratin molecules are held together by means of covalent disulfide linkages, salt linkages between basic side chains (e.g. arginine and lysine) and acidic side chains (aspartic and glutamic acids), hydrogen bridges, ester linkages (e.g., between serine and glutamic acid residues), and van der Waals forces of attraction between comparatively inactive side chains. The polypeptide sheets or grids formed in this manner are further held together in bundles by hydrogen bonding, as well as van der Waals forces.

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[120] Pandit, unpublished work; see also Ioffe, Kekkonen, and Kalita, *J. Gen. Chem. U.S.S.R.* **14,** 816 (1944).

[121] Stoves *in* Fibrous Proteins, Society of Dyers and Colourists, 1946.

[122] Coleman and Hewitt *in* Fibrous Proteins, Society of Dyers and Colourists, 1946.

Arginine	$H_2N—C(=NH)—NH—CH_2CH_2CH_2CH(NH_2)—COOH$
Lysine	$H_2N—CH_2CH_2CH_2CH_2CH(NH_2)—COOH$
Aspartic acid	$HOOC—CH_2CH(NH_2)—COOH$
Glutamic acid	$HOOC—CH_2CH_2CH(NH_2)—COOH$

The fine structure of wool, like that of cellulose, consists of both crystalline and amorphous regions. A distinguishing feature of the wool fiber in comparison with cellulose or silk is that unstretched wool (α-keratin) gives an X-ray pattern different from stretched wool (β-keratin), the latter resembling the pattern for silk. If stretched in cold water, the transformation is reversible, and when stretched wool is released in water, the X-ray photograph now corresponds to the unstretched fiber. The identity period along the fiber axis in α-keratin is about 5.15A, and in β-keratin about 6.66A; the repeat is at 7A in silk. The α- → β-keratin transformation involves an extension of the polypeptide chains by about 100%. Some kind of coiling of the polypeptide chains in α-keratin has therefore to be assumed, but the precise nature of the coils is still controversial.[124]

From an analysis of the water adsorption isotherm, it has been calculated that the fraction of wool which is inaccessible to water, and which is considered to be the crystalline phase, is a little less than half of the whole.[125] The average diameter of the pores in water-swollen wool is 35 to 41A, which is of the same order as the estimated pore diameter of cellulose fibers.[126] The relatively small molecules of acid dyes readily enter and diffuse through the pores of the disorganized regions of the wool fiber when it is swollen by the action of hot water. The swelling increases with increasing temperature, and the maximum absorption of dyes takes place at or near the boil. The dye molecules under these conditions are able to migrate freely from pore to pore throughout the fiber, and level dyeing takes place. On cooling, the swelling process is reversed and the pores return to more or less their original size. If the dyed fiber is treated with boiling water, swelling again takes place, followed by diffusion of the dye molecules or "bleeding" into the water. The comparatively low wash-fastness of the level dyeing type of acid dyes on wool and direct dyes on cotton is therefore to be anticipated. The larger the dye molecule, the less freedom will it have to migrate to and from the intermicellar spaces, and in general, the less will be the level dyeing character and the greater the fastness to washing. Speakman and Clegg have related levelling properties to the colloidal character of the dyes in solution; the less the tendency to aggregate the greater the levelling power; the tendency of a dye to become colloidal in the acid dyebath increases with the molecular weight and decreases with degree of sulfonation.[126] Improved fastness to washing, so far as this is concerned with the mechanical imprisonment of the dye within the fiber pores, might conceivably result from an increase in the particle size of the dye by aggregation. Azoic and vat dyes on cotton aggregate as a result of soaping, but there is no experimental evidence of acid dyes undergoing aggregation within the fiber in the usual method of applying acid dyes to wool, which merely consists in treatment with a boiling solution of the dye in presence of sulfuric acid and Glauber salt. On the other hand, acid dyes on wool have considerably higher washing fastness than direct dyes on cotton. The fiber-dye attachment must therefore be of a more stable type. When a mordant dye is applied to wool in conjunction with chromium, there are two distinct factors which lead to a decrease in levelling power and an increase in washing fastness. The first is that a complex of chromium and the azo dye is formed, which is much larger in size than the unmetallized dye. The second factor is chemical combination between fiber, dye and chromium.

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[123] Harris and Brown *in* Fibrous Proteins, Society of Dyers and Colourists, 1946.

[124] Huggins, *Chem. Revs.* **32,** 195 (1943). See also Consden, Gordon, and Martin, *Biochem. J.* **44,** 548 (1949); Mizushima *et al.*, *Nature* **164,** 918 (1949).

[125] Hailwood and Horrobin, Symposium of the Faraday Society on Swelling and Shrinking, 84 (1946).

[126] Speakman, *Proc. Roy. Soc. London* **A132,** 167 (1931); Speakman and Clegg, *J. Soc. Dyers Colourists* **50,** 348 (1934).

The existence of ionic bonds in wool between amino and carboxyl groups in side chains of neighboring keratin molecules provides a simple and essentially correct picture of the mechanism of dyeing wool with acid dyes in presence of an acid such as sulfuric acid. Hydrogen ions diffuse into the fiber and neutralize the anionic charges of the carboxyls. Electrical neutrality is then maintained by the diffusion of anions into the fiber; the more mobile sulfate ions (from sulfuric acid and from Glauber salt) diffuse more rapidly into the fiber than the heavier dye anions. Both types of anions compete for the cationic charges of the ammonium groups in the fiber, and the amount of dye ultimately adsorbed depends on a variety of factors such as the affinity of the dye anions and the concentrations of acid and Glauber salt.[127]

Although the acid dyes are organic compounds of molecular weight of the order of several hundreds, the dye acids, which usually contain one to three sulfonic groups, are strong acids; K_a for many of them[128] is 10^{-1} to 10^{-2}, comparable to trichloroacetic acid and to sulfuric acid with respect to the dissociation of the second hydrogen. The capacity of wool for combination with hydrochloric and other simple acids provides, therefore, an indication of the quantitative relationship between fiber and dye in dyeing wool with acid dyes. When wool is titrated with hydrochloric acid, combination is complete at pH 1, when 80 milliequivalents of acid per 100 g. of dry wool have been absorbed.[129] The amount of combined acid may be roughly correlated with the basic side chains of the α,ϵ-diamino acid (lysine), the guanidine derivative (arginine) and the imidazole derivative (histidine). The precise mechanism of the reaction between wool and acid is however by no means clear. One explanation has been in terms of equilibria involving the wool fiber with an internal ionic bond and wool in combination with an external anion or a proton or both.[130] Gilbert and Rideal[131] consider this to be unsatisfactory, and derive an equation involving the potential on the fiber during adsorption of acid under various conditions. The Gilbert-Rideal equation has been found to hold for the system Orange II acid-wool.[132] The affinity of Orange II acid for wool is 10.3 kcal per mole at 60°; 6 kcal are due to the H ions and the balance to the dye anions.[132] Using the measurements of

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[127] Elöd, *Trans. Faraday Soc.* **31,** 305 (1935).

[128] Ender and Müller, *Melliand Textilber.* **18,** 906 (1937); see also *ibid.* 633, 732, 809, 991.

[129] Speakman and Stott, *Trans. Faraday Soc.* **31,** 1425 (1935).

[130] Steinhardt and Harris, *J. Research Natl. Bur. Standards U.S.* **24,** 335 (1940).

[131] *Proc. Roy. Soc. London* **182A,** 335 (1944); Gilbert, *ibid.* **183A,** 167 (1944).

[132] Meggy, *Trans. Faraday Soc.* **43,** 502 (1947). The absorption of monobasic acid dyes by nylon can be accounted for by the Gilbert-Rideal mechanism; Remington and Gladding, *JACS* **72,** 2553 (1950).

Speakman and Clegg,[126] Gilbert has found that among four pairs of dyes which differed in the replacement of a benzene by a naphthalene ring the affinity increased by 1.1–1.5 kcal. The introduction of an additional sulfonic group decreased the affinity by 0.9–1.0 kcal.[131]

Lemin and Vickerstaff[133] have defined the affinity of acid dyes for wool in terms of the change in standard chemical potential of the dye during adsorption on the fiber. They have developed equations by which the affinity can be evaluated from equilibrium measurements of (a) the adsorption of free dye acids by wool, (b) the displacement of dye anions from dyed wool by inorganic anions, and (c) the competition between two dyes for the sites in the wool fiber. For the six dyes they studied the different methods yielded consistent affinity values; but the anion affinities of all the six dyes (the azo dyes Naphthalene Orange G, Metanil Yellow YK, Coomassie Red G; and the anthraquinone derivatives Solway Ultra Blue B, Solway Purple R and Solway Blue R) varied only within the range -4.2 to -7.0 kcal, and they cannot be correlated with the differences in the chemical constitution or the dyeing properties and wash fastness of the dyes. Peters has studied the effect of an alkyl chain on affinity by measuring the adsorption of a series of dyes of two types containing an alkyl chain of increasing length; the affinity increased almost linearly with chain length and the increment per methylene group was 400 cal in both types.[133a]

Peters and Speakman have found 8000 to be the average molecular weight of the fraction of wool which does not pass into solution during treatment with chlorine peroxide to break the cystine cross-linkages.[134] The presence of such short protein chains and the consequent availability of the terminal amino groups indicate an acid-combining capacity which is much larger than the value of 80 milliequivalents per 100 g. dry wool, which is observed by following the pH of the solution when wool is treated with acid, and which is accounted for by the basic side chains of lysine, arginine and histidine. By studying the pH value within the fiber which can be calculated although it cannot be measured directly, Peters and Speakman find that even the side chains and the terminal amino groups taken together cannot account for the observed acid-combining capacity; and they consider[135] that the Donnan membrane equilibrium provides a much more precise interpretation of the acid dyeing of wool than the Gilbert-Rideal theory.[134, 136]

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[133] *J. Soc. Dyers Colourists* **63,** 405 (1947). A generalized approach to the problem of the adsorption of acids, bases and dyes by the protein fibers is presented by Vickerstaff in Ref. 1*a*; the treatments due to Elöd, Speakman, Gilbert and Rideal, and others are then derived and the differences discussed.

[133a] Unpublished work quoted by Vickerstaff in Ref. 1*a*.

[134] *J. Soc. Dyers Colourists* **65,** 63, 285 (1949); *Dyer* **99,** 71 (1948).

[135] See also Elöd, *Trans. Faraday Soc.* **29,** 327 (1933).

While there is some evidence to show that the combination of wool with acid dyes is stoichiometric and corresponds to the combining capacity for simple acids,[128, 137] several facts suggest a more complicated mechanism for the acid dyeing process. One is the observation of Astbury that X-ray analysis of wool saturated with acid dye sometimes shows the presence of free crystalline dye.[137a] The dye anions do not penetrate the crystallites, but Speakman and Elliott have found that the crystalline phase of wool is relatively rich in amino acids with basic side chains.[138] They have shown that phenol-2,4,6-trisulfonic acid combines as a tribasic acid with wool, so that electrical neutrality of the fiber is achieved by polyvalent ions acting at a distance from some at least of the basic side chains of the fiber. Combination of wool with acid dyes may thus be stoichiometric in spite of the impenetrability of the crystalline phase; the crystallites are penetrated by protons and an equivalent number of dye anions are adsorbed on the surface of the micelles to achieve electrostatic balance. Such a system would not be in accord with Pauling's principle[139] that electrical neutrality has to be established locally on the smallest possible scale,[140] but Speakman considers that micellar subdivision and the electron mobility in proteins[124, 141] might be the explanation. As a result, dye anions are present in the fiber partly by ionic binding with basic side chains in the amorphous phase, and partly by adsorption on the surface of the crystallites. Wool fibers may be more or less permanently set (or maintained in the stretched condition) by stretching under the action of boiling water or steam, and X-ray examination of the setting properties of dyed fibers has shown that the fiber-dye combination has an orientating influence on the structure. Speakman suggests that this might arise from partial subdivision of the micelles, to which may also be ascribed the tendering of wool when it is dyed very heavily.[142, 143] The combination of wool with acids of high

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[136] Contrast Kitchener and Alexander, *J. Soc. Dyers Colourists* **65,** 284 (1949); *Textile Research J.* **20,** 203; 481 (1950).

[137] Smith and Harris, *J. Research Natl. Bur. Standards U.S.* **19,** 81 (1937).

[137a] Textile Fibres under the X-rays, ICI (Dyestuffs).

[138] Speakman and Elliott, *in* Fibrous Proteins, Society of Dyers and Colourists, 1946.

[139] *JACS* **51,** 1010 (1929).

[140] Barrer, *in* Fibrous Proteins, Society of Dyers and Colourists, 1946.

[141] Denbigh, *Nature* **154,** 642 (1944).

[142] Goodall and Hobday, *J. Soc. Dyers Colourists* **55,** 529 (1939); Steinhardt and Fugitt, *J. Research Natl. Bur. Standards U.S.* **29,** 315 (1942).

[143] Skinner and Vickerstaff, *J. Soc. Dyers Colourists* **61,** 193 (1945).

affinity can result in considerable hydrolysis of amide side chains,[144] and although there are no grounds for believing that this takes place under normal conditions of dyeing, the high reactivity of the disulfide and amide linkages in a protein indicates that chemical changes in the wool fiber during dyeing cannot be altogether excluded.

It is important to remember that the absorption of protons, as a result of which the wool fiber would acquire cationic activity and a consequent attraction for dye anions, is not a necessary step through which dyeing with acid dyes has to proceed, since there are acid dyes which are substantively absorbed at pH values higher than the isoelectric point of wool.[145] The acid dyes vary widely in their substantivity to wool, just as there are marked differences in the substantivity of dyes to cellulose; and a relationship has been noticed[144] between the molecular weights of a series of organic acids and their affinities for wool. While the absorption of a dye such as Orange G (aniline → G-acid; M.W. 452), which forms a true solution in water, is very similar to that of hydrochloric acid, the colloidal dye Polar Yellow R (a pyrazolone dye containing a *p*-toluenesulfonyl ester group; M.W. 832) is absorbed at 100° to a maximum extent of 140 milliequivalents per 100 g. of wool.[142] Although mechanical factors such as the molecular dimensions of the dyes in comparison with the pore diameters in the amorphous regions of the wool fiber may be involved, the character of the protein or mixture of proteins constituting keratin is sufficient to show that, apart from union by means of direct or long range ionic affinities, dye molecules can attach themselves to wool by means of van der Waals forces or hydrogen bonding.[146]

Alexander and Charman[146a] have recently studied the adsorption by wool of a dye having a long hydrocarbon chain (Carbolan Crimson BS, ICI; an alkyl derivative of Azo Geranine 2GS or Kiton Yellow S, CI 637). The kinetic curves indicated an initial rapid, but limited, reaction which was followed by a much slower reaction. The magnitude of the initial adsorption was correlated with the surface activity of the solution; the dye was located on the fiber surface which, being largely nonpolar, was an interface for adsorption of surface-active substances.

Wool has affinity not only for acid dyes and basic dyes by virtue of the basic and acidic side chains in the keratin molecule, but like cellulose, wool has affinity also for the leuco compounds of sulfur dyes and vat dyes, and for the anilides of *o*-hydroxycarboxylic acids in alkaline solution.

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[144] Steinhardt, Fugitt, and Harris, *J. Research Natl. Bur. Standards U.S.* **26**, 293 (1941); **28**, 191, 201 (1942); **29**, 417, 425 (1942).

[145] Cf. Elöd and Reutter, *Melliand Textilber.* **20**, 57 (1939).

[146] Cf. Valko, *J. Soc. Dyers Colourists* **55**, 173 (1939).

[146a] *Textile Research J.* **20**, 761 (1950).

The infrared absorption spectrum indicates the occurrence of hydrogen bonds in proteins, and the basis for the structure of proteins in general is the formation of multiple hydrogen bonds between neighboring polypeptide chains.[147] The denaturation of proteins is due to the breaking of these cross-linkages and the absorption of dyes by protein fibers is in part a similar phenomenon in which the intermolecular hydrogen bonds between the keratin molecules are replaced by hydrogen bonds between keratin and dye. From this point of view it is clear that the presence of hydrogen-bonding groups is a structural factor in a dye molecule which is favorable to affinity for cellulose and protein fibers alike.

[147] Huggins, *Ann. Rev. Biochem.* **11,** 27 (1942). See also Rodebush, "The Hydrogen Bond" *in* Advances in Nuclear Chemistry and Theoretical Organic Chemistry, Interscience Publishers, New York, 1945; Hunter, *Annual Repts. Chem. Soc. London* **43,** 141 (1946).

CHAPTER XLII

IDENTIFICATION, ANALYSIS, AND EVALUATION OF DYESTUFFS

The identification of a commercial dyestuff as a known dye or mixture of dyes is important for the users of dyestuffs, public analysts and chemical examiners in customs laboratories. Because of the very large number of dyestuffs marketed under a much larger number of names, the problems of identification and analysis have become exceedingly complex.[1–5a] The chemical identity of a dye is of interest to the color user, since two dyes giving the same shades on dyeing may differ substantially in fastness properties, but chemical identity is often more difficult to establish than identity or similarity in dyeing and fastness properties. The prerequisite for the chemical analysis of dyes is a knowledge of their constitution, so that this is one of the many points of view from which work on the chemistry of commercial dyes is of the utmost scientific and practical value. It is clear from a consideration of the number and variety of the synthetic dyes that their analysis, especially in mixtures, can never become a simple routine. Identification of a dye as belonging to a chemical or dyeing class is relatively easy, but complete proof of identity with a dye of known constitution is much more difficult. Since many of the distinguishing tests depend on color reactions, an important requirement for success in dyestuff analysis is the possession of a complete range of authentic samples with which a direct comparison can be made. A wide and intimate knowledge of the physical, chemical and dyeing properties of dyes is a valuable asset to the dyestuff analyst; and valuable circumstantial evidence of the nature of the dyes present in dyed textiles and other colored materials, which frequently enables short cuts to be

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[1] Gallup, Joyce, Fierz-David and Yarsley, Allen's Commercial Organic Analysis, Vol. VI, 5th ed., Churchill, London, 1933.

[2] Green, The Analysis of Dyestuffs, 3rd ed., Griffin, London, 1920; reprinted with "Key to trade designations," 1941.

[3] Zühlke, Analyse von Farbungen, Dr. Max Janecke Verlagsbuchhandlung, Leipzig, 1937.

[4] Clayton, Identification of Dyes on Textile Fibres, *in* Thorpe's Dictionary of Applied Chemistry, 4th ed., Vol. IV, Longmans, London, 1940.

[5] Identification of dyestuffs in IG, *BIOS* **763.**

[5a] For an account of the purification and estimation of dyes from the point of view of work on the fundamental processes of dyeing, see Vickerstaff, The Physical Chemistry of Dyeing, Oliver and Boyd, London, 1950.

taken in routine procedures, can be obtained if the analyst is familiar with dyeing and coloring practice in the relevant industries.

Methods for the chemical analysis of dyes have been briefly indicated during the systematic treatment of dyes in accordance with the chemical classification, the methods being dependent on the constitution of the dyes and the presence of reactive groups. Thus azo dyes can be usually estimated by titration with titanous chloride, some basic and acid dyes by titration with each other or with ions of opposite character so as to form insoluble complexes, and certain indigoid dyes by sulfonation and titration with permanganate. The only method applicable to vat dyes as a class is to determine the amount of vattable constituent by alkaline reduction and reoxidation. Direct chemical methods of analysis are frequently impracticable and of very limited value in dealing with commercial dyes. Colorimetric and spectroscopic methods, and dye-trials or evaluation procedures based on the application of the dyes, are therefore widely employed. Dyes which are insoluble in water and the common organic solvents and are of unknown constitution, such as the sulfur dyes, can only be evaluated by dye-trials.

Some commercial dyestuffs, such as basic dyes, azoic coupling components (particularly the amines), and a few of the anthraquinonoid acid and vat dyes, are of high purity, but dyes in general are not marketed in the pure state. The manufacturers and users of dyestuffs are interested in products of standard quality giving reproducible results in application rather than in their chemical purity. Commercial dyes are therefore standardized in shade, concentration and physical form, so that dyers and other color consumers may be able to produce a definite effect with a given quantity of a dye. Two types of impurities or substances other than the essential tinctorial constituent occur in commercial dyes: (1) by-products of the various reactions by which the dye is synthesized and (2) the substances (e.g., sodium chloride and sulfate, dextrin, dispersing agents) added subsequently for standardization. Among the latter may be one or more dyes added to the main dyestuff for shading purposes. The inorganic diluents (e.g. common salt, Glauber salt, sodium carbonate) can obviously be separated from water-insoluble dyes by mere treatment with water. Complete separation of soluble azo dyes from inorganic salts is not easy; two methods are used: (1) precipitation of the dye from a saturated aqueous solution by means of sodium acetate and extraction of the sodium acetate by boiling absolute alcohol, these processes being repeated until the dye is analytically pure; and (2) crystallization of the salts formed with di-*o*-tolylguanidine and regeneration of the sodium salt by treatment of the methanolic solution with the calculated amount of sodium methoxide (see Chapter XI). The first method often gives low yields; the second has not been adequately investigated. The free acids of some acid and direct cotton dyes can be precipitated from aqueous solution by hydrochloric or sulfuric acid, crystallized, and neutralized exactly with aqueous caustic soda. Dyes containing sulfonic groups are very hygroscopic and difficult to dry; drying at 100° (or higher, if the dye does not decompose) in an Abderhalden vacuum drying apparatus over phosphorus pentoxide, until all the moisture has been removed, is therefore necessary before the dyes are submitted to elementary analysis. Basic dyes are often readily crystallizable, specially as the zinc chloride or other double salts. Methods of purification of sulfur, vat, and other classes of dyes have been mentioned in the relevant chapters.

The separation of a mixture of two or more dyes from each other presents much more intractable problems than the separation of a dye from inorganic or colorless organic substances. The first step is to determine qualitatively if a given dyestuff is homogeneous or is a mixture of dyes. The dry powder is blown on to filter paper wetted with water or a water-miscible solvent such as alcohol or cellosolve. Acetone is useful for cellulose acetate dyes. Sodium sulfide solution may be used for wetting the paper in examining sulfur dyes. Differently colored spots, which may be examined for individual dyes by color reactions, indicate a mixture. Blowing the dyestuff powder on to the surface of concentrated sulfuric acid in a porcelain dish is another test, since many dyes give characteristic colorations with sulfuric acid. Neither of these tests is satisfactory for dyes which have not been mixed as dry powders, but in aqueous solution and then dried down. The capillary test,[6] suggested by Schönbein in 1862, is more useful for such dyestuffs, especially when the principles and technique of chromatographic adsorption analysis are applied. In the old procedure one end of a strip of filter paper was dipped into a dilute solution of the dyestuff in water or other solvent; after a few minutes different colored zones appeared, if the differences in the capillary attraction and in the affinity of the constituent dyes for cellulose were sufficiently marked. Fractional dyeing, carried out by immersing one-inch square pieces of fabric successively in the dyestuff solution at intervals of half a minute, is another useful procedure for separating the dyes in a mixture. A mixture of acid dyes may be thus applied to wool from an acetic acid or formic acid bath. It is necessary to remember, however, that a commercial dyestuff mixture is likely to be made up of single dyes which have very similar affinities for a fiber. Extraction of the dyestuff with alcohol, ether, chloroform, amyl acetate or other organic solvent is useful for separation, if the constituents differ in their solubilities; an aqueous solution of the dyestuff may be extracted with water-immiscible solvents. The dye acids from acid dyes and the dye bases from basic dyes may be liberated by neutralization before extraction; and the acidification or basification can be carried out fractionally. Thus, when an aqueous solution of a mixture of the three basic dyes Rhodamine, Magenta and Safranine is extracted with ether, a colorless ether solution of the Rhodamine base is obtained; addition of ammonia and ether extraction then gives the Magenta base; and final basification with caustic soda followed by ether extraction gives the Safranine base.[7]

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[6] Goppelsroeder, Capillaranalyse, Birkhäuser, Basel, 1906; see also *J. Soc. Dyers Colourists* **4,** 5 (1888); Rheinboldt, Capillar- und Adsorptionanalyse *in* Houben, Die Methoden der Organischen Chemie, Vol. I, 3rd ed., Georg Thieme, Leipzig, 1925.

Partition between immiscible solvents, using a fractionation procedure based on a countercurrent principle, is sometimes effective for the separation of dyes from a mixture.[8] Thus a mixture of Naphthol Yellow S, Orange I and Indigo Carmine can be separated in the following manner. An aqueous hydrochloric acid solution is shaken through three funnels containing amyl alcohol. The amyl alcohol solution is washed repeatedly with dilute hydrochloric acid. Indigo Carmine is obtained in the aqueous extract. The amyl alcohol is then washed repeatedly with salt solution, when Orange I is obtained. Naphthol Yellow S is estimated by difference. Separation of dyes by means of immiscible solvents has been thoroughly investigated with the limited range of dyes used for coloring foods, drugs and cosmetics.[9,10] Relative solubility in various organic solvents and in water of graded pH also serves as a basis for the separation of dyes into groups, to which the other methods outlined later can then be applied for a closer identification.[8]

Mixtures of dyes in aqueous solution can be separated by frothing with gelatin at different pH values.[11] Basic and acid dyes can be separated by means of ion-exchange resins.[12]

CHROMATOGRAPHY

Chromatography was discovered in 1906 by Tswett, a Russian botanist, in connection with the isolation of green leaf pigments. Although he drew attention to the wide applicability of his new technique, a quarter-century elapsed before it was recognized to be a powerful and versatile method for separating mixtures into their components. The power of chromatography in solving separation problems is shown by the classic example of the carotenoids; seven carotenoids were known in 1922, and over seventy have now been isolated.

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[7] Rota, *Chem. Ztg.* **22,** 437 (1898).

[8] Mathewson, *Am. Dyestuff Reptr.* **37,** 709 (1948); and earlier references quoted in this paper.

[9] Woodman, Food Analysis, 4th ed., McGraw-Hill, New York, 1941.

[10] Koch, *J. Assoc. Offic. Agr. Chemists* **26,** 245 (1943).

[11] Aenlle, *Anales fis. y quim. Madrid* **42,** 179 (1946).

[12] Griessbach, *Angew. Chem.* **52,** 215 (1939).

A detailed treatment of the theory and practice of chromatography, of which there are three main types (adsorption chromatography, ion-exchange chromatography, and partition chromatography), is beyond the scope of this book, and reference must be made to the many excellent books and reviews that are available.[13a–i] An elementary account is given from the point of view of the applications of chromatography to coal-tar constituents, intermediates and dyes.

The use of charcoal and other adsorbents for the removal of impurities from a substance in solution has long been common practice; chromatography is a countercurrent or differential adsorption, analogous to distillation with a fractionating column which enables separations to be effected that are not possible by a straight distillation. Chromatographic separations are primarily dependent on the reactive groups in molecules, while fractional distillation is effective in separating molecules which differ in size. The characteristic of chromatography, which distinguishes it from the older technique of separation by means of adsorbents or by partition between solvents, is that a dynamic distribution of a solute between two phases (a solution and a solid adsorbent or a solution and an immiscible liquid) is achieved by the passage of one phase through a second stationary phase.

Adsorption chromatography. The technique of adsorption chromatography usually consists of three stages. (1) A solution of the mixture under examination is poured down a column of an adsorbent, the com-

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[13a] For references before 1942 see Zechmeister and Cholnoky, Principles and Practice of Chromatography, 2nd ed., Chapman and Hall, London, 1941; Strain, Chromatographic Adsorption Analysis, Interscience, New York, 1942.

[13b] Tiselius *in* Advances in Colloid Science, Vol. I, Interscience, New York, 1942.

[13c] Hesse, Adsorptionsmethoden im chemischen Laboratorium, DeGruyter, Berlin, 1943.

[13d] Zechmeister, Progress in Chromatography 1938–1947, Chapman and Hall, London, 1950.

[13e] Cassidy and others, Chromatography, *Ann. N. Y. Acad. Sci.* **49,** 141–326 (1948).

[13f] Lederer, Progrès Récents de la Chromatographie, Première Partie, Chimie Organique et Biologique, Hermann, Paris, 1949.

[13g] Chromatographic Analysis, *Discussions of the Faraday Soc.* **7,** 1–336 (1949).

[13h] Strain *in* Frontiers in Colloid Chemistry, Interscience, New York, 1950; *Anal. Chem.* **21,** 75 (1949); **22,** 41 (1950); **23,** 25 (1951).

[13i] Cassidy, Adsorption and Chromatography *in* Technique of Organic Chemistry, Vol. V, Interscience, New York, 1951.

monest until recently being activated alumina, charged in a glass tube of appropriate dimensions. Solvents for chromatography must be purified very carefully. Nonpolar solvents such as the hydrocarbons and some of the chlorinated hydrocarbons (e.g. methylene chloride, chloroform, carbon tetrachloride) are the most suitable; but under certain conditions a wide range of solvents is permissible. Thus, pterins have been separated by adsorption on alumina columns, using $0.004N$ aqueous or methanolic hydrochloric acid (Becker and Schöpf, 1936). (2) The chromatogram is "developed": the adsorbed material is separated into differently colored bands by washing through with a solvent. The original solvent may be adequate for effecting the separation of the constituents into zones; or movement of the bands may be facilitated by using a more polar solvent or by the addition of a small amount (often as small as one per cent) of a more polar solvent (e.g. alcohol). The sharpness and speed of separation depend on complex solute-adsorbent, solute-solvent and solvent-adsorbent relationships. Hesse arranges solvents in the following order in terms of decreasing strength of adsorption of a solute: petroleum ether, carbon tetrachloride, trichloroethylene, benzene, methylene chloride, chloroform, ether, ethyl acetate, acetone, *n*-propanol, ethanol, methanol, water, pyridine.[13c] (3) The adsorbates in the various zones are recovered or eluted in one of two ways. By washing the column with a suitable solvent or series of solvents, the zones are progressively pushed down and the solute is recovered from the corresponding percolate; alcohol and other hydrogen-bonding solvents are good eluants. A "liquid chromatogram" is thus obtained.[13a] Alternatively, the adsorbent column is removed from the glass tube in which it is supported, and each zone is cut out and extracted with a solvent. Boiling hydrochloric acid in acetone has been used for eluting 5-hydroxyflavone from the yellow zone of the lake which it forms on an alumina column (Karrer and Schwab, 1941).

Elution, frontal and displacement analysis. Besides the commonly practised elution analysis outlined above, there are two main methods for the development of chromatograms (or chromatographic analysis): frontal analysis and displacement analysis, both due to Tiselius (1940, 1943); the conditions for the successful operation of a column are quite different for these three types.[13g] Frontal analysis consists in forcing a solution through an adsorbent column, previously washed with pure solvent, determining the concentration of the effluent, and plotting it against the volume; characteristic curves showing one "step" for every solute are thus obtained. In displacement development the substances to be separated are adsorbed at the top of the column and a solution of a substance wlth stronger adsorption is forced through the column; the latter acts as a developer which displaces the substances to be separated, which also displace each other. The concentration of the effluent is plotted against the volume, and by measuring the heights and lengths of the steps both qualitative and quantitative analyses of the constituents in the mixture are achieved, provided a developer is found that will displace the unknown mixture quantitatively. The Tiselius techniques, elaborated by Claesson and others, are particularly valuable for the separation of colorless compounds and for using such adsorbents as carbon; the concentration of the constituents in the percolate is followed continuously by means of the refractive index, electrical conductivity or other physical property. Claesson has shown that by frontal analysis quantitative analysis of as many as six fatty acids (e.g. n-C_8, C_9, C_{10}, C_{12}, C_{14}, C_{16}) in a mixture is possible.[13e] The technique of displacement development can also be used in ion-exchange chromatography and partition chromatography (see later).

Adsorbents. Although the choice of an adsorbent is still partly empirical, there is increasing knowledge of the suitability of an adsorbent for separating certain types of substances, and some examples of the specific use of adsorbents are cited. An adsorbent is chosen which exhibits as high a selectivity as possible among the components of the mixture that is to be separated; the available solvents partly determine the choice of the adsorbent. Alumina and other oxides are effective for compounds containing polar groups. Alumina, calcium hydroxide, zinc carbonate and calcium carbonate are the adsorbents generally used for the isolation of the carotenoids, and their adsorbing capacity decreases in the stated order. Strain has studied the adsorption sequence of certain carotenoids on columns of sugar, of Celite, and of magnesia. Relative adsorbability was determined largely by the selective affinity of the adsorbents for groups or parts of the pigment molecules. Sugar preferentially attracted the polar hydroxyl groups of the xanthophylls; and magnesia the unsaturated parts of carotenes and xanthophylls, as well as the hydroxyls of the latter.[14] Using a column of magnesia for studying the separation of xanthophylls and chlorophylls, Strain has shown that many conditions influence the distribution of solutes within their adsorption zones; thus a pigment which usually yields a single colored zone may yield two zones in the presence of certain colorless contaminants. Powdered magnesium sulfate has been used for the separation of carbonyl compounds as the 2,4-dinitrophenylhydrazones.[14a] Brockmann has shown that water-soluble salts, such as copper and zinc sulfate, are useful adsorbents for the chromatographic separation of azobenzene derivatives; aluminum sulfate can be used for the separation of the hydroxyanthraquinones, and compounds very firmly adsorbed can be isolated merely by dissolving the adsorbent in water.[13g]

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[14] *JACS* **70,** 588 (1948); *Ind. Eng. Chem.* **42,** 1307 (1950).

[14a] Stadtman, *JACS* **70,** 3583 (1948).

Silica gel formed in the presence of methyl, ethyl, propyl and butyl orange has been found to be 4 to 20 times as effective in adsorbing the particular dye as a control gel; decreasing adsorption is shown for dyes with decreasing similarity of molecular structure.[14b] This observation may prove to be of great value for the separation and purification of water-soluble dyes.

Carbon has the advantage that it can be prepared and activated by a variety of methods; it is a commonly used decolorizing agent and absorbent for solvent recovery, and it has now found application in chromatography by frontal and displacement analysis. Examples of its uses are the resolution of a mixture of mono-, di- and trisaccharides,[14c] the separation of amino acids,[14d] the measurement of the adsorption isotherms of aliphatic acids,[14e] and an investigation of high molecular substances.[14f]

Allowing for the specificity of adsorbent action, Strain arranges adsorbents in the following order of increasing activity: sucrose, starch; inulin; magnesium citrate; talc; sodium carbonate; potassium carbonate; calcium carbonate; calcium phosphate; magnesium carbonate; magnesia (Merck); lime (freshly and partially slaked); activated silicic acid; activated magnesium silicates; activated alumina, charcoal, magnesia (Micron brand); Fuller's earth.[13a] With a given adsorbent, the activity can be varied by processes of activation (e.g. heat or solvent treatment) or deactivation (e.g. washing with water or an alcohol for which the adsorbent has affinity). The adsorbent can then be graded by examining the separation of a standard mixture; Brockmann and Schodder have employed binary mixtures of azobenzene and its derivatives (e.g. *p*-amino-, *p*-hydroxy- and *p*-methoxyazobenzene), dissolved in benzene and petroleum ether, for measuring the adsorptive capacities of activated alumina.[13a] A ternary mixture of azobenzene, benzeneazo-β-naphthol and *p*-dimethylaminoazobenzene dissolved in chlorobenzene-petroleum ether can be used.[15] Müller has determined the heat of wetting of alumina by solvents and has used it for grading the activity of the adsorbent.[16]

Chemical changes, reversible or irreversible, can occasionally occur during column chromatography.[17] Certain carotenoids adsorbed on acid earths from non-polar solvents form a deep blue zone (cf. the color reactions with sulfuric acid and antimony trichloride) on the top of the column, but on elution with alcohol the color change is reversed and the carotenoid is recovered unchanged. Meunier and Vinet have suggested that the color is due to polar resonance structures resulting from the donation of electrons by the carotenoid molecule to the adsorbent. Triarylmethyl halides form colored complexes when adsorbed on silica gel, apparently because of the polarization of the dye on the polar surface of the adsorbent; elution with alcohol gives the colorless or pale colored non-polarized triphenylmethane derivatives (Weitz and Schmid, 1939). Examples of irreversible changes are the conversion of vitamin A to anhydro vitamin A, rearrangement of the double bond system in vitamin D_2, loss of biological activity when vitamin K_1 is adsorbed on alumina or magnesia (but not on sugar), and catalytic oxidation of vitamin C on charcoal.[13a, d] Acetone passed through an alumina column gives appreciable amounts of diacetone alcohol (Hesse, 1938).[13a] When anthracene in light petroleum as solvent and developer is chromatographed on an alumina column with exposure to light, dianthracene can be isolated from the column. When naphthacene is adsorbed on an alumina column from benzene solution and developed with the same solvent, the column becomes yellow and the side exposed to the window light turns orange, owing to the formation of a quinone.[17a] The picrates and trinitrobenzene compounds of some aromatic hydrocarbons, terpenes and steroids break up during passage through an alumina column; picric acid or trinitrobenzene remains adsorbed, and the hydrocarbon is obtained in the percolate (Kondo, 1937).[13a] Zechmeister has discussed the precautions necessary in chromatographing labile compounds.[13e]

[14b] Dickey, *Proc. Natl. Acad. Sci. U.S.* **35,** 227 (1949).

[14c] Whistler and Durso, *JACS* **72,** 677 (1950).

[14d] Tiselius and Hagdahl, *Acta. Chem. Scand.* **4,** 394 (1950).

[14e] Nestler and Cassidy, *JACS* **72,** 680 (1950); see also Hagdahl and Holman, *ibid.* 701; *J. Biol. Chem.* **182,** 421 (1950).

[14f] Claesson in Ref. 13g.

[15] Cropper, *J. Soc. Dyers Colourists* **61,** 162 (1945).

[16] *Helv. Chim. Acta* **26,** 1945 (1943); **27,** 404 (1944). See also Trueblood and Malmberg, *Anal. Chem.* **21,** 1055 (1949); LeRosen *et al., ibid.* **22,** 811 (1950).

Development of colorless substances. For following the separation of colorless substances, various devices are known: one is prior conversion into colored derivatives. Strain used the dinitrophenylhydrazones for carbonyl compounds, and examples of azo dyes are cited later. Zones of acids have been identified by pretreatment of the adsorbent with an indicator. In Zechmeister's "brush method" the column is extruded and a camel-hair brush dipped in a suitable reagent is drawn down the side of the column so that a narrow colored streak is produced. The two forms of stilbene, 4,4′-dimethyl- or 4,4′-dimethoxystilbene separate on alumina, the *trans* above the *cis* with a broad interzone; the zones can be located by streaking with one per cent permanganate along the column.[13d]

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[17] For a review, see Meunier and Vinet, Chromatographie et mésomérie. Adsorption et résonance, Masson et Cie, Paris, 1947.

[17a] Levy and Campbell, *JCS* 1445 (**1939**).

Proteins separated on filter paper or a cellulose column have been located by dyeing with acid dyes not staining cellulose.[17b] Color reactions of various kinds have been utilized for visualizing zones of separation on filter paper, and by analogy with photographic development, the "development" of a chromatogram of colorless substances often refers to the process of visualization, rather than the separation of the zones. Using ultraviolet light the fluorescence of substances or their ability to quench fluorescence can be employed for the identification of zones. Naphthalene, anthracene and the more complex polycyclic hydrocarbons (e.g. perylene, 1,2-benzpyrene), as well as carbazole, acridine and other heterocyclic compounds occurring in coal tar, have been separated in the pure state from samples of the substances prepared and purified by the usual methods of isolation and crystallization; the chromatograms are examined in ultraviolet light, and the zones separated by taking advantage of the differences in the fluorescence colors (Winterstein).[18] Zechmeister has tabulated a long series of polycyclic hydrocarbons which have been purified by chromatography on alumina.[13d] Fluorescent zinc sulfide can be used for following the quenching of fluorescence; and alcohols (C_1–C_6) have been separated as their 3,5-dinitrobenzoates from hexane on silica gel pre-treated with Rhodamine 6G, using hexane-ether for development and ether for elution.[19] Colorless non-fluorescing compounds can be converted into fluorescent derivatives, e.g. fatty acids into *p*-phenylphenacyl esters.[20] Radioactivity has been used for locating zones along columns and on filter paper. When such methods for locating zones are unavailable or inconvenient, the column is washed through with a solvent; the percolate is collected in fractions (using automatic fraction-collecting equipment, if necessary), and the successive fractions are estimated in terms of a physical property such as the pH,[13a] refractive index, or electrical conductivity.[13b] Chemical analysis (e.g. acid-base titration), antibacterial tests, and physiological assay methods can also be used.

[17b] Jones and Michael, *Nature* **165,** 685 (1950). Several new streak reagents are suggested by LeRosen *et al.*, *Anal. Chem.* **22,** 809 (1950). In "surface chromatography" a powdered adsorbent, fixed rigidly to a microscope slide by means of a suitable binder, provides a convenient system for microchromatography; mordant dyes have been used as ripening agents for developed chromatograms of cations in surface chromatography; Meinhard and Hall, *Anal. Chem.* **21,** 185 (1949); *ibid.* **22,** 344 (1950).

[18] Winterstein *et al.*, **Ber.** 68, 1079 (1935); and earlier papers. See also Almasy, *Biochem. Z.* **291,** 421 (1937). Vahrman has separated and estimated the hydrocarbons in primary tars by chromatography on a column of silica heated by steam; *Nature* **165,** 404 (1950).

[19] Sease, *JACS* **69,** 2242 (1947); White and Dryden, *Anal. Chem.* **20,** 853 (1948).

[20] Kirchner *et al., Ind. Eng. Chem. Anal. Ed.* **18,** 31 (1946).

Chemical constitution and chromatographic behavior. Molecules which differ in the nature, number and position of the polar groups (in which double bonds and aromatic ring systems are included) are in general readily separable by simple adsorption chromatography.[20a] *Cis-trans* isomers can be separated. Molecules which differ only in the size of non-polar groups (e.g. the homologous fatty acids) are difficult to separate. Chromatography has proved successful in resolving racemates by means of asymmetric adsorbents.

Correlations between chemical constitution and chromatographic behavior can only be attempted in molecules of the same or similar type and under specified conditions of chromatographic treatment. Changes in the sequence of adsorption of the constituents in a mixture have been observed, both when the adsorbent is changed and when the developing solvent is changed. Thus Strain was able to separate some ternary mixtures in four of the six possible sequences by changing the solvent;[21] and LeRosen found that cryptoxanthin is above lycopene on alumina and on calcium carbonate columns, but the order is inverted on a column of calcium hydroxide, using benzene as developer with all the three adsorbents.[22] An inversion of the sequence of adsorption of *N*-ethyl-*N*,*N'*-diphenylurea and 4-nitro-*N*-ethylaniline was observed by Schroeder when a slight alteration in the composition of the developer (2 or 5% of ethyl acetate in light petroleum) was made.[13e] LeRosen defines the adsorption affinity R as the rate of movement of the adsorptive zone (mm./min.) divided by the rate of flow of developing solvent;[22] R corresponds to R_F used in partition chromatography (see later). R values have been used for standardizing adsorbents and for determining the efficiency of developers; using the same adsorbent and solvent, R values provide a quantitative measure of the adsorption affinities of a series of compounds which can then be correlated with their chemical constitution.

The relation between constitution and adsorbability has been thor-

[20a] According to Sinomiya, functional groups influence adsorbability in the following decreasing order: COOH or OH, NH_2, NO_2, Me, H; *J. Chem. Soc. Japan* **61,** 1221 (1940).

[21] *Ind. Eng. Chem. Anal. Ed.* **18,** 605 (1946).

[22] LeRosen, *JACS* **64,** 1905 (1942); *et sequa.* LeRosen *et al., Anal. Chem.* **23,** 730, 732 (1951), have recently attempted to construct a mathematical function relating the interactions in the chromatographic system to the movement of the adsorptive zone. The adsorption could be accounted for in terms of donor-acceptor and hydrogen-bonding interactions; the carbon side chain decreased adsorption. Donor values were assigned to O and N, and hydrogen-bonding values to OH and NH. The solvents were assigned arbitrary values as competitive agents, and the adsorbent strengths were experimentally evaluated. Rates of movement of chromatographic zones calculated on the basis of assigned values agreed reasonably well with experimental values.

oughly investigated in the carotenoid group (Winterstein and Stein; Kuhn; Karrer; Zechmeister). Double bonds, esterified hydroxyl groups, carbonyl groups and hydroxyl groups influence the adsorption in the given order of increasing effect. The strength of adsorption increases with the number of each group. Conjugated double bonds produce stronger adsorption than isolated double bonds. A carbonyl group conjugated with a double bond produces stronger adsorption than the separated groups.

Winterstein has studied the relation between adsorbability and constitution among aromatic hydrocarbons. The strength of adsorption increases with the number of benzene rings, if there are no other complicating factors. Linear molecules are more strongly adsorbed than those with angular or condensed ring systems. Anthracene is more strongly adsorbed than phenanthrene. Chrysene (4 rings, 9 double bonds) is more strongly adsorbed than pyrene (4 rings, 8 double bonds). Naphthacene (4 rings) is more strongly adsorbed than chrysene (4 rings), 1,2-benzpyrene (5 rings), and 1,2,6,7-dibenzanthracene. Larger polarizability increases the strength of adsorption, and since it also increases light absorption deeper colored hydrocarbons are in general found in higher zones in a Tswett column. 1,2,6,7-Dibenzanthracene (orange-yellow) is less strongly adsorbed than naphthacene (orange), but more strongly than 1,2,5,6-dibenzanthracene (colorless). Perylene (orange-yellow) is more strongly adsorbed than 1,2-benzpyrene (pale yellow). While correlations of the carcinogenic activity of hydrocarbons with their structure, absorption spectra and chemical reactivity have been suggested, no attempt appears to have been made to look for any relationship with their adsorbability, for instance on protein adsorbents.

By repeated chromatography on an alumina column, using petroleum as solvent and petroleum-methanol as eluant, anthracene (Kahlbaum) was shown by Winterstein to contain at least 0.05 per cent of carbazole, as well as naphthacene and anthraquinone. Purified anthracene exhibits an intense blue fluorescence, suppressed by the addition of one part of naphthacene in 3,000,000. Commercial chrysene was shown to contain 1,2-benzocarbazole and naphthacene; and "pure pyrene" to contain brasan (2,3,5,6-dibenzocoumarone), naphthacene and 2,3,6,7-dibenzophenanthrene. Winterstein and Vetter isolated 2.5 g. of the carcinogenic hydrocarbon, 1,2-benzpyrene, from 3.5 kg. of a coal-tar fraction boiling above 450°.[22a]

Wieland and Probst (1937) found that a mixture of fluorene and

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[22a] Chromatography on alumina from light petroleum has shown that commercial 1,2-benzpyrene is contaminated with 1′,2′,3′,4′-tetrahydro-1,2-benzpyrene; Cook and Schoental, *Nature* **167**, 725 (1951).

9-methylfluorene formed isomorphous crystals which appeared to be homogeneous; the m.p. of the dibromo derivative was constant. The fact that the substance was a mixture became apparent only by chromatography on alumina, fluorene being more strongly adsorbed than the homolog. Repeated chromatography gave pure fluorene with a very faint fluorescence in ultraviolet light.

Chromatography is useful for quality control in dye intermediates, for the preparation of intermediates in the pure state for special purposes, and for the qualitative and quantitative separation of impurities in dye intermediates such as the amines, naphtholsulfonic acids and aminonaphtholsulfonic acids.

The three nitroanilines have been separated by adsorption on a column of lime, the *para* compound being most strongly adsorbed and the *ortho* the least (Karrer and Nielsen, 1934).[22b] The nitrophenols are also adsorbed in the order *para, meta* and *ortho*, the adsorbability being proportional to the dipole moments.[23] 3-Nitro-*o*-4-xylenol is more strongly adsorbed by silicic acid than the 5-nitro isomer.[23a] The adsorption of a series of nitro compounds on a column of silica gel mixed with Celite 535 has been studied by Schroeder[13e] and by Ovenston[24] in connection with the analysis of explosives; alumina is valueless for the purpose. Schroeder observed that on silicic acid inversions in the sequence of adsorption by change of developer occurred very frequently; several compounds exhibited the undesirable effect of "double zoning"—the production of two zones when each of two zones of a mixture separated chromatographically is eluted and re-chromatographed. Using benzene-ligroin or ether-ligroin for development, Schroeder made the following generalizations about the effect of the number and position of substituent groups on the relative adsorption affinity of diphenylamine and its derivatives. Diphenylamine was very weakly adsorbed, 2-nitrodiphenylamine slightly more strongly, and 4-nitrodiphenylamine much more strongly. Chelation of the 2-nitro with the imino group was regarded as being responsible for the low adsorption affinity of the 2-nitro compound, an effect so marked that the 2,2′,4-trinitro and 2,2′,4,4′-tetranitro derivatives were less strongly adsorbed than 4,4′-dinitrodiphenylamine.[24a] An *N*-nitroso group was able either to increase or

[22b] See also Trueblood and Malmberg, *JACS* **72,** 4112 (1950).

[23] Arnold, *JACS* **61,** 1611 (1939).

[23a] Holler *et al., JACS* **72,** 2036 (1950).

[24] *J. Soc. Chem. Ind.* **68,** 54 (1949).

[24a] The influence of intramolecular hydrogen bonding, and of hydrogen bonding between the adsorbed compound and the adsorbent (silicic acid), on the adsorption affinities of derivatives of diphenylamine and *N*-ethylaniline has been studied by Schroeder; *JACS* **73,** 1122 (1951).

decrease adsorption affinity, as shown by the following increasing order of adsorbability: diphenylamine, *N*-nitrosodiphenylamine, *N*-nitroso-4-nitrodiphenylamine, 4-nitrodiphenylamine. Using 1–35% of acetone in light petroleum for development, Ovenston found that the following compounds separated in the stated order of increasing adsorbability: 1-nitronaphthalene; 2,4,6-trinitroxylene; 1-chloro-2,4-dinitrobenzene; 2,4-dinitrotoluene; 1,3-dinitrobenzene; 2,4,6-trinitrotoluene; 2,4,6-trinitrophenetole; 1,3,5-trinitrobenzene; 2,4,6-trinitroanisole; 2,4-dinitroanisole; 2,4,6-trinitrophenylethylnitramine; 2,4,6-trinitrophenylmethylnitramine (tetryl); 1,3,8-trinitronaphthalene; 2,4,6-trinitro-*m*-cresol; 2,4,6-trinitrophenol; 2,4,6,2′,4′,6′-hexanitrodiphenylamine; 2,4-dinitrophenol; 2,4-dinitroresorcinol; 2,4,6-trinitroresorcinol. The influence of an increasing number of nitro and hydroxyl groups in increasing adsorbability, and the influence of *O*-alkyl groups in decreasing adsorbability are in accordance with anticipation; further, a nuclear alkyl group decreases the adsorption affinity.

Benzidine is more strongly adsorbed on alumina than α-naphthylamine,[25] an effect apparently related to the shape of the molecules as well as the extra amino group in benzidine. β-Naphthol is more strongly adsorbed than α-naphthol, and 2-naphthol-4-sulfonic acid more strongly adsorbed than 1-naphthol-4-sulfonic acid (NW-acid)[25] because of the readier accessibility of the β-hydroxyl group for hydrogen bonding with the adsorbent.

Examining the chromatographic separation of a series of hydroxyanthraquinones on silica gel, Hoyer found that anthraquinones containing hydroxyl groups in the α-positions, because of chelation with the CO groups, percolated readily through the column. The position of the hydroxyl groups was more important than the number, as shown by the fact that 2-hydroxyanthraquinone remained adsorbed on the column, while 1,4,5,8-tetrahydroxyanthraquinone passed through.[25a]

If a mixture of 1- and 2-aminoanthraquinones, dissolved in toluene-pyridine, is passed through a column of suitably prepared alumina, and developed with toluene-pyridine, the 1-isomer washes through completely, while the 2-isomer is retained; the violet zones at the top of the column are probably due to the presence of 1,2- and 1,4-diaminoanthraquinones in technical 1-aminoanthraquinone.[15] Stewart has examined the relation between constitution and chromatographic behavior of simple anthraquinone derivatives.[13g] Subject to the qualification that a change in the activity of the adsorbent by water addition altered the order of movement of the bands, the order of increasing adsorption for mono-substitution was halogen, arylamino, alkylamino, amino, acylamido, side-chain hydroxyl, and nuclear hydroxyl group. Adsorption generally increased with increase in the number of substituent groups, and adsorption from aqueous solution decreased with increase in the number of sulfonic groups. There was no systematic relation between mono-substitution in the 1- and 2-positions. It will be clear from the results reported below[26] that the order of separation of acylamidoanthraquinones depends on the position of the substituent and on the presence or absence of an *N*-alkyl group.

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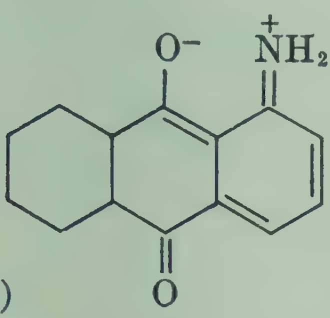
[25] Ruggli and Jensen, *Helv. Chim. Acta* **18,** 624 (1935); **19,** 64 (1936); Ruggli and Stäuble, *ibid.* **23,** 689 (1940). See also Ruiz, *Ind. parfum.* **1,** 187 (1946).

[25a] *Kolloid-Z.* **116,** 121 (1950).

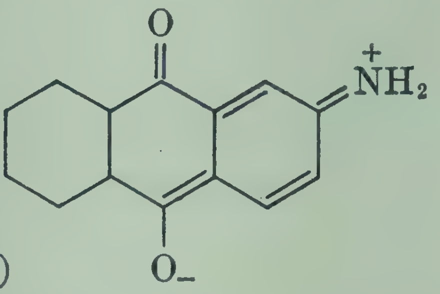
When a series of aminoanthraquinones are chromatographed on alumina, using benzene as solvent for adsorption and development, the strength of adsorption is in the following increasing order: anthraquinone, *N*-methyl-1-aminoanthraquinone, 1-benzamidoanthraquinone, 1-aminoanthraquinone, 1,5-diaminoanthraquinone, 1,8-diaminoanthraquinone, *N*-methyl-1-benzamidoanthraquinone, 2-benzamidoanthraquinone, 2-aminoanthraquinone, 1,4-diaminoanthraquinone, 1,4,5-triaminoanthraquinone, 1,2-diaminoanthraquinone, 1,4,5,8-tetraminoanthraquinone, 2,6-diaminoanthraquinone.[26] These aminoanthraquinones are useful for the standardization of alumina, because they are available commercially, they are easy to purify by crystallization and chromatography, and mixtures separate in distinctly colored zones. The increase in adsorbability with the number of amino groups in the α-aminoanthraquinones is to be anticipated; the depth of color increases in the same order. As Hoyer found with the hydroxyanthraquinones, the position of the amino groups is important, but there is a difference between the two substituents in that the position is not the over-riding factor when the number of amino groups is increased beyond two. The proton-donor properties of the NH_2 group are known to be less than those of the OH group, and infrared spectra indicate that powerful hydrogen bonding as between the OH and CO groups in the hydroxyanthraquinones does not exist between the NH_2 and CO groups in the aminoanthraquinones, but weak hydrogen bonding is not ruled out.[27] Apparently, the chelation of the α-amino group is strong enough to make the β-amino group more readily available for hydrogen bonding with alumina, resulting in the greater strength of adsorption of β-aminoanthraquinone. However, chelation in the α-aminoanthraquinones is so weak that in 1,4-diaminoanthraquinone (and to an increased extent in 1,4,5-triamino- and 1,4,5,8-tetraminoanthraquinone) the availability of amino groups for hydrogen bonding with alumina is sufficient to render them more strongly adsorbed

[26] Rao, Shah and Venkataraman, *Proc. Indian Acad. Sci.* **34A,** 355 (1951).
[27] Flett, *JCS* 1444 (**1948**).

than 2-aminoanthraquinone, but insufficient for increasing the strength of adsorption above that of 2,6-diaminoanthraquinone. The greater strength of adsorption of 1,8-diaminoanthraquinone in comparison with the 1,5-isomer is understandable in view of the independent chelation of each NH_2 with a CO group in the latter compound. Another approach to the relative adsorbabilities of 1- and 2-aminoanthraquinones is to consider the resonance interaction between the NH_2 and one of the CO groups; in the resonance structures (I) and (II) the α-compound will have a considerably smaller dipole moment than the β-, and the strength of adsorption will be correspondingly smaller. The effect of *N*-benzoylation is to decrease the strength of adsorption of both 1- and 2-aminoanthraquinones, but for two somewhat different reasons. In α-aminoanthraquinone *N*-acylation would increase the strength of the chelation between the 9-CO and NH groups; and in β-aminoanthraquinone *N*-acylation would decrease the resonance interaction between the 10-CO and NH groups. Two reasons may be suggested for the stronger adsorption of 1,4-diaminoanthraquinone in comparison with the 1,8-compound as well as β-aminoanthraquinone. The influence of the polarization shown in (I) will be to increase the proton-donor character of the NH_2 group in the 4-position; and the symmetrical distribution of polarities in 1,4-diaminoanthraquinone probably favors adsorption.



(I)



(II)

An important achievement by the use of chromatographic technique was the separation of *cis*-azobenzenes from the common *trans* compounds.[28] Using an alumina column and benzene as solvent and developer, *cis*-azobenzene remains on the column and the *trans* compound passes through. When a mixture of the stable form and the two unstable forms of 4-benzeneazo-azobenzene is chromatographed, the most strongly adsorbed is the *cis-trans* form, the *cis-cis* form separates as an intermediate zone, and the *trans-trans* form is least strongly held.[28]

2,2′-Bismethylmercaptoazobenzene and the corresponding azoxy compound have been separated by chromatography on alumina from benzene solution; the azoxy compound is more strongly adsorbed.[28a]

Anils prepared from the nitrotoluenes and *p*-nitrosodimethylaniline have been separated on alumina. When the product of the condensation of 4-methyl-3-nitroazobenzene with *p*-nitrosodimethylaniline is chromatographed from benzene solution on alumina, the unchanged azo compound appears in the benzene percolate; elution of the major orange-brown and violet-brown zones with acetone gives the *p*-dimethylaminoanilide of 3-nitroazobenzene-4-carboxylic acid and the *p*-dimethylaminoanil of 4-aldehydo-3-nitroazobenzene.[28b]

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[28] Cook, *JCS* 876 (**1938**); Zechmeister, Frehden and Fischer-Jorgensen, *Naturwissenschaften* **26,** 495 (1938).

[28a] Simons and Ratner, *JCS* 421 (**1944**).

Chromatography of dyes. The advantages of chromatography are now well known: its value as a test for purity; ability to separate a complex mixture of compounds having only minor differences in structure; rapidity; simplicity and ready availability of the equipment; applicability to micro quantities for purposes of isolation, identification and quantitative estimation of the constituents of a mixture, as well as large quantities for preparative purposes; and usefulness in isolating very small quantities of solutes from very large volumes of solutions. The formation and movement of bands in chromatographic adsorption have been submitted to theoretical and mathematical treatments; using cellulose and fibrous proteins as adsorbents, the chromatography of dyes may throw new light on the affinity of dyes for fibers. Considering the scope for chromatographic investigations in the synthetic dyestuff field, surprisingly little work has been carried out so far. One difficulty in dealing with many dyes is that the choice of solvents is very limited. Dyes are divisible into two classes from the point of view of solubility: water-soluble and water-insoluble. The water-soluble dyes (e.g. the very numerous group of azo dyes) are in general insoluble in the organic solvents; on the other hand, the water-insoluble dyes (e.g. sulfur dyes and anthraquinonoid vat dyes) are usually insoluble or very sparingly soluble in the cold in solvents suitable for chromatography.

Chromatographic homogeneity is an especially valuable test for the purity of a dye. Certain medicinal dyes (Pellidol; Rivanol; Trypaflavine) have been shown to be impure by the formation of several bands when adsorbed on columns of alumina (Franck, 1937). Ruggli and Jensen[25] found that commercial Congo Red could be obtained chromatographically homogeneous after a few crystallizations from aqueous alcohol. According to Haller, Congo Red chromatographed on precipitated calcium carbonate was fractionated into two parts (an intensely colored blue adsorbate and a red percolate), attributed to different degrees of dispersion.[13a] Commercial Benzoazurine G (dianisidine $\rightrightarrows$ NW-acid, 2 moles) gave a dark blue band at the top and a broad light blue zone which dyed cotton shades similar to those from the commercial dye, a grayish blue filtrate dyeing violet shades faster to ironing than the commercial dye shades, and a red filtrate at the bottom. The change from blue-violet to red was attributed to polymerization; similar effects were obtained by ironing a dyed fabric, warming a solution of the dyestuff, or adding alcohol to the solution. Commercial trisazo and tetrakisazo dyes gave complex chromatograms, indicating the difficulty of obtaining homogeneous dyes when third and fourth diazonium couplings are involved.[25] Using Brockmann's alumina and Clarit (a bleaching earth) as adsorbents, and benzene as solvent and developer, coloring matters (e.g. Martius Yellow, Sudan III, Scarlet R, Fat Ponceau) in oils and fats have been separated and detected (Thaler, 1937).

[28b] Chardonnens and Heinrich, *Helv. Chim. Acta* **22,** 1471 (1939); **23,** 1399 (1940).

Ruggli and Jensen[25] have separated mixtures of azo, basic and acid dyes, and have traced interesting relationships between the constitution of certain azo dyes and the adsorbability. Alumina washed with a very dilute solution of lime was found to have improved adsorptive powers; calcium carbonate was also suitable as an adsorbent. The solvent used for adsorption and development was usually water. The zones were separated and eluted with boiling water. The adsorbability was related to the number of azo groups, so that ready separation of a mixture was possible if the dyes differed in the number of azo groups. Examining a mixture of the trisazo dye Diamine Green, the disazo dye Congo Red, and the monoazo dye Diamine Rose FFB, it was found that adsorption took place in the order named. A similar observation was made with a series of dyes prepared by diazotizing and coupling J-acid with itself successively. The adsorbabilities of the disazo dyes prepared by coupling tetrazotized benzidine with two molecules of each of five aminonaphtholsulfonic acids were in the following order: 2,8,6 (γ-acid); 2,5,7 (J-acid); 6,2,4; 1,8,4 (S-acid); and 1,5,7 (M-acid). Thus the β-naphthylamine derivatives were more strongly adsorbed than the α-naphthylamine derivatives, so far as the sulfonic acids examined and the particular conditions of adsorbent and solvent were concerned. *o*-Hydroxyazo dyes were more strongly adsorbed than the *p*-isomers, while the sodium sulfonates of 1-arylazo-2-naphthols and the corresponding 2-arylazo-1-naphthols had about the same adsorbability. When *o*-hydroxy- and *p*-hydroxyazo compounds free from sulfonic groups were examined, using quinoline or benzene as solvent, the effect of the hydroxyl groups was reversed, the *p*-compound being more strongly adsorbed than the *o*-isomer. The influence of a hydroxyl group not chelated with an azo group in promoting adsorption on alumina is also shown by an observation made on azo dyes from resorcinol.[29] When a mixture of 4-benzeneazoresorcinol and 2,4-

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[29] Gore, Panse and Venkataraman, *Proc. Indian Acad. Sci.* **29A,** 289 (1949). See also Bhate, Panse and Venkataraman, *ibid.* **32A,** 360 (1950); Gore and Venkataraman, *ibid.* **34A,** 368 (1951).

or 4,6-bisbenzeneazoresorcinol is chromatographed on alumina from a solution in benzene or chloroform, the monoazo compound is more strongly adsorbed and constitutes the upper zone, in sharp contrast to the behavior of the monoazo dye (Diamine Rose) and the disazo dye (Congo Red) mentioned earlier. 4,6-Bisbenzeneazoresorcinol is more strongly adsorbed than the 2,4-isomer, indicating stronger chelation of the two hydroxyls with the azo groups in the latter compound; a structure in which each of the two chelate rings contains two double bonds can be written only for 2,4-bisbenzeneazoresorcinol. This is in conformity with the observation of Baker *et al.* that 2,4-diacetylresorcinol is more strongly chelated than the 4,6-isomer.[30] 4-Benzeneazoresorcinol is more strongly adsorbed from chloroform solution than 2-benzeneazoresorcinol, the very weak adsorption of the latter being due to the chelation of both the hydroxyls with the azo group. A mixture of 4,6-bisbenzeneazoresorcinol, 2-benzeneazoresorcinol, and 2,4-bisbenzeneazoresorcinol in chloroform separates in this order of decreasing adsorbability.

Coupling α-naphthylamine with diazonium salts, the 2- and 4-azo compounds are formed in about 7 and 93% yields respectively; they can be separated by chromatographic adsorption on alumina, the *p*-compound being more strongly adsorbed.[30a]

Ruggli and Jensen found that Erika B and Erika G, which are very similar monoazo dyes in which the same diazonium salt (from dehydrothio-*m*-4-xylidine) is coupled with ϵ-acid and G-acid respectively, were inseparable; but ready separation could be effected between the two closely related disazo dyes Direct Sky Blue (dianisidine $\rightrightarrows$ H-acid, 2 moles) and Direct Blue 2B (benzidine $\rightrightarrows$ H-acid, 2 moles), the two methoxyl groups apparently causing the difference. Again, Cloth Fast Black B (1-naphthylamine-5-sulfonic acid → 1-naphthylamine → phenyl peri-acid) and Cloth Fast Blue R (aniline → Cleve acid → phenyl peri-acid) had identical adsorbability. Unlike cotton, alumina did not distinguish between the substantive Congo Red type of dyes and the corresponding unsubstantive dyes from *m*-substituted benzidines.[25]

A combination of electrophoresis and chromatographic adsorption is sometimes more effective than the latter alone, and mixtures of dyes (e.g. Methyl Orange, Methyl Red and Indigo Carmine) adsorbed on Tswett columns have been separated by applying an electrical potential; this method is also useful for studying the tautomerization of indicators.[31]

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[30] *JCS* 1689 (**1934**).

[30a] Turner, *JCS* 2282 (**1949**).

[31] Strain, *JACS* **61,** 1292 (1939). Hanson and Gould, *Anal. Chem.* **23,** 670 (1951), have reported that Strain's procedure gave unsatisfactory results with a mixture of three monoazo dyes, and they have obtained excellent separations on talc-

The conversion of a colorless compound into an azo dye is useful for its chromatographic separation. Amines may be diazotized and coupled. For compounds capable of coupling with a diazonium salt, this reaction offers a simple device as it does for their colorimetric estimation. The presence of α-naphthol in β-naphthol, G-acid in R-acid, and of isomeric compounds and by-products in various other intermediates can thus be detected and quantitatively estimated. Estrone, estradiol and estriol have been separated after coupling with a diazonium salt.[31a] Chromatography of the *p*-phenylazobenzoyl esters has been used for the separation of sugars (and of sterols).[31b] Methyl esters of amino acids have been separated by chromatographic adsorption of the *N*-azobenzene-*p*-sulfonyl derivatives on alumina treated with a 10% solution of acetic acid in methanol.[31c] Cholic and desoxycholic acids have been separated after esterification by means of ω-bromo-*p*-methylazobenzene.[31d] Ethyl esters of amino acids give with azobenzene-*p*-isocyanate colored derivatives that are separable on alumina.[31e]

Ruggli and Jensen found that Fluorescein and its halogenated derivatives were adsorbed in the following order: Rose Bengal (Cl_2I_4); Erythrosine (I_4) and Phloxine (Cl_4Br_4); Eosine (Br_4) and Spirit Eosine (methyl ester of Eosine); Fluorescein. Nine basic dyes were adsorbed in the following order: Victoria Blue B; Methylene Blue D and Patentphosphine G; Crystal Violet 5BO and Fuchsine and Safranine OO; Brilliant Green and Malachite Green; Auramine. Of 36 binary mixtures of these dyes, 32 were separable, the remaining four being Auramine and Malachite Green; Brilliant Green and Malachite Green; Patentphosphine and Methylene Blue; Fuchsine G and Safranine. A ternary mixture of Auramine, Victoria Blue and Methylene Blue (or Fuchsine) could be separated.[25] A mixture of ignited alumina (14 parts) and Hyflo Supercel (one part), wetted with a buffer solution of primary and secondary potassium phosphate (each 0.002*M*), has been used for demonstrating the application of chromatography to the separation of three basic dyes, Victoria Blue B, Crystal Violet and Auramine, from 95% ethanol.[32]

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powdered glass and on talc-Super-Cel with or without potential applied to the electrodes. Thus by adsorption from an aqueous solution and development and elution with aqueous pyridine Congo Corinth and Congo Red, as well as several other pairs of azo dyes, were separated.

[31a] Heftmann, *Science* **111,** 571 (1950).

[31b] Reich, *Biochem. J.* **33,** 1000 (1939); Coleman *et al., JACS* **65,** 1588 (1943); *ibid.* **67,** 381 (1945); Ladenburg, Fernholz, and Wallis, *J. Org. Chem.* **3,** 294 (1938).

[31c] Reich, *Biochem. J.* **43,** No. 3, Proc. XXXVIII (1948).

[31d] Silberman and Silberman-Martyncewa, *J. Biol. Chem.* **165,** 359 (1946).

[31e] Masuyama, *J. Agr. Chem. Soc. Japan* **23,** 45 (1949).

[32] Rieman, *J. Chem. Education* **18,** 131 (1941).

Instead of a solid adsorbent, foams (gas-liquid interfaces) and emulsions (liquid-liquid interfaces) can be used for the fractionation of mixtures; Abribat observed that Methyl Violet could be separated by foam into a top fraction of the hexamethyl derivative (Crystal Violet) and a lower red-purple fraction.[32a]

Oxazine dyes obtained by the condensation of β-naphthol-3,6- and 6,8-disulfonic acids with *p*-nitrosodimethylaniline have been chromatographed in 80% alcohol on alumina, using water and (for the 6,8-compound) M/15-potassium dihydrogen phosphate for elution.[33]

In a homologous series of cyanine dyes of the Astraphloxine type, derived from 1,3,3-trimethylindolenine, the adsorbability increases with the number of double bonds, so that the tricarbocyanine, dicarbocyanine, carbocyanine and cyanine are adsorbed on alumina in this order.[25] It is generally observed that in compounds of a given chemical type those exhibiting longer wave length and higher intensity absorption appear at the top of the column.

The relative degree of adsorption of a series of common indicators on Silene FF (a commercial hydrated calcium silicate) has been determined, using 90% dioxane as solvent and developer.[33a]

A notable application of chromatography is in the isolation of naturally occurring hydroxyanthraquinones. Eight hydroxyanthraquinone derivatives (see Chapter XXVIII) have been isolated from the bark of *Coprosma lucida* by repeated chromatographic adsorption from acetone solution on calcined magnesia.[34] Emodin (1,6,8-trihydroxy-3-methylanthraquinone), aloe-emodin (1,8-dihydroxy-3-hydroxymethylanthraquinone) and iso-emodin (2,5,8-trihydroxy-3-methylanthraquinone) occurring in *Cascara sagrada* separate in the stated order from top to bottom of a column of magnesia-Celite, using chloroform as solvent for adsorption and development; after elution of the bands with hydrochloric acid (to dissolve the magnesia) and chloroform, quantitative estimation of the constituents can be carried out spectrophotometrically.[35]

Cis- and *trans*-thioindigo and *cis-* and *trans*-5,5′-dichloro-4,4′,7,7′-tetramethylthioindigo have been separated from benzene solution on a silica gel column.[35a] Ruggli and Stäuble found that Indigosols were very weakly adsorbed on alumina or calcium carbonate; Indigosol Pink IR extra (the Indigosol from 6,6′-dichloro-4,4′-dimethylthioindigo), Indigosol O and Indigosol 04B (from tetrabromoindigo) appeared in the percolate in the order named.

[32a] USP 2,313,007; Abribat *et al.*, Sur les phénomènes de mouillabilité et les applications de ces phénomènes, Hermann, Paris, 1942; Eastman Kodak, BP 535,099. For a review see Shedlovsky, *Ann. N. Y. Acad. Sci.* **49,** 279 (1948).

[33] Eggers and Dieckmann, *Biochem. Z.* **310,** 233 (1942).

[33a] Karabinos and Hyde, *JACS* **70,** 428 (1948).

[34] Briggs and Nicholls, *JCS* 1241 (**1949**). See also Howard and Raistrick, *Biochem. J.* **46,** 49 (1950).

[35] Gibson and Schwartling, *J. Am. Pharm. Assoc. Sci. Ed.* **37,** 206 (1948).

[35a] Wyman and Brode, *JACS* **73,** 1487 (1951).

It has been claimed that vat dyes in nitrobenzene solution can be separated on alumina,[36] but many vat dyes are insoluble or very sparingly soluble in nitrobenzene (and other organic solvents) in the cold. Conflicting statements on the separability of alkaline vats on alumina have been made.[36, 37, 38] Vat dyes reduced by aqueous caustic soda and hydrosulfite have been chromatographed on columns of bleached sawdust or disintegrated cotton; the chromatogram was then developed in the colors of the oxidized dyes by means of potassium ferricyanide solution.[36] This method appears to be limited to the separation of dyes of widely different substantivity to cellulose.

A generally applicable method for the separation of vat dyes[39] is to vat the mixture of dyes with aqueous tetraethylenepentamine, $NH_2(CH_2CH_2NH)_3CH_2CH_2NH_2$, and hydrosulfite, carry out the adsorption on a column of cellulose powder (80 mesh),[40] and develop the chromatogram with aqueous tetraethylenepentamine containing a little hydrosulfite.[41] One part of the organic solvent and four parts of water are employed both for adsorption and development. A clear and remarkably stable vat is obtained when a vat dye is made into a paste with tetraethylenepentamine and treated with aqueous hydrosulfite at room temperature (23–30°). Employing these conditions, the following mixtures have been separated; the dyes in each mixture are mentioned in the order of increasing adsorbability, the last dye being at the top of the column: (1) Caledon Gold Orange G and dibenzanthrone; (2) Caledon Yellow 3G and Caledon Brilliant Purple 4R; (3) Caledon Yellow 3G, Caledon Jade Green, Caledon Red BNS and dibenzanthrone. *n*-Butylamine, which has been recommended as an effective solvent in conjunction with hydrosulfite for stripping vat dyes,[8] gives a clear vat in the absence of caustic soda, but *n*-butylamine is less effective than tetraethylenepentamine in separating a mixture of vat dyes by chromatography on a cellulose column.

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[36] Johnson quoted in Vickerstaff, The Physical Chemistry of Dyeing, Oliver and Boyd, London, 1950.

[37] Fox, Vat Dyestuffs and Vat Dyeing, Chapman and Hall, London, 1946.

[38] Bilik, *Novosti Tekhniki* No. 42–43, 42 (1936).

[39] Rao, Shah and Venkataraman, *Current Sci. India* **19,** 149 (1950); **20,** 66 (1951).

[40] Pulped filter paper and powdered cellulose have been previously used as a bulking agent in column chromatography and as a support in partition chromatography; Wachtel and Cassidy, *JACS* **65,** 665 (1943); Hough, Jones and Wadman, *Nature* **162,** 448 (1948).

[41] Belen'kii, *Zavodskaya Lab.* **14,** 403 (1948), has mentioned that tetraethylenepentamine is a useful solvent for dyes.

Paper chromatography ("Papyrography").[41a] Cellulose in the form of filter paper is of exceptional interest, and has been widely studied in recent years. The term "paper chromatography" is at present employed for chromatographic separations on paper in general, regardless of the mechanism of separation; and it therefore includes paper partition chromatography (see later). For dyestuffs the technique of paper chromatography is essentially a refinement of Schönbein's "capillary analysis." Placing a drop of the dyestuff solution on filter paper, followed by a few drops of water, is sometimes adequate for effecting a separation into concentric zones of the individual dyes. As long ago as 1893 Paterson[42] thus obtained a "remarkably defined capillary spectrum" of purple-black, orange, green and yellow from the commercial dyestuff Brilliant Black E; he also measured "capillary speeds" and showed that dyes containing sulfonic groups (e.g. Acid Magenta) had higher speeds than basic dyes (e.g. Magenta). Grundy[43] described a scheme for the identification of colors in dyed paper based on successive extractions with boiling water, ethanol and ammonia to separate acid, basic and direct dyes respectively; capillary technique using blotting paper or acetate silk was then employed for the separation of individual dyes. The capillary phenomena exhibited by dye solutions and sols were investigated by Garner.[44] By measuring the percentage rise R of the dyestuff solution on filter paper in comparison with that of the solvent, he classified dyes into four groups: (i) acid dyes of low molecular weight ($R = ca$ 100); (2) moderately well-levelling acid dyes, neutral wool dyes and some very soluble direct dyes ($R = ca$ 70); (3) well-levelling direct dyes ($R = ca$ 40); (4) poor levelling direct dyes, insoluble mordant colors and some dispersed acetate silk dyes ($R = ca$ 10).

A convenient procedure is to use a rectangular or semicircular filter paper with a short stem in the middle (Fig. 1) which is dipped in the dyestuff solution (a few cc. in a crystallizing dish); after a few minutes the dyestuff solution is replaced by the developing solvent. Carried out under standard conditions of size and quality of the filter paper, the concentration of the solution, the heights to which the component with the highest capillary activity is allowed to rise before and after the introduction of the developing solvent (lines AB and CD in Fig. 1) and other

[41a] The instruments and techniques used in paper chromatography have been reviewed by Clegg, *Anal. Chem.* **23**, 396 (1951); **22**, 48 (1950).

[42] *J. Soc. Dyers Colourists* **9,** 110 (1893).

[43] *Proc. Tech. Sect. Paper Makers Assoc. G. B. and Ireland,* **14,** 233 (1933).

[44] *J. Soc. Dyers Colourists* **49,** 346 (1933). See also Yokoyama, *J. Pharm. Soc. Japan* **63,** 492 (1943).

factors, reproducible results can be obtained. The paper and solution must not be exposed to draughts, and it is convenient to have the set-up inside a balance case provided with some arrangement (such as double lengths of thin wire or string) for supporting a series of paper strips. The method is useful for acid dyes which separate into sharp and definite bands; e.g. a mixture of the four acid dyes, Naphthol Green B, Tartrazine NS, Solway Blue BS and Orange II (order of increasing adsorbability) can be separated, water being used for adsorption and development.[39]

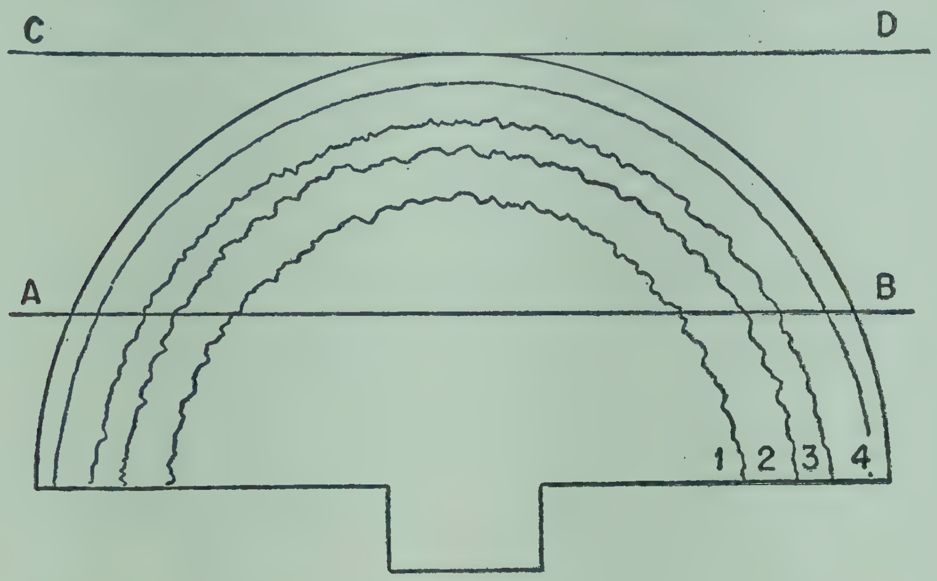

Fig. 1. Filter-paper chromatogram of four acid dyes. (1) Orange II; (2) Solway Blue BS; (3) Tartrazine NS; and (4) Naphthol Green B.

Basic and direct dyes,[45, 45a] do not separate into sharp bands from an aqueous or dilute acetic acid solution; but clear separations can be effected when a 1:4 mixture of water and methyl cellosolve acetate is used for adsorption and development.[39] Thus the following mixtures have been separated: (a) Methylene Blue, Safranine and Auramine O; (b) Chrysophenine CH, Congo Red, and Chlorazol Sky Blue FF. Auramine O is more strongly adsorbed than Brilliant Green in contrast to their behavior on alumina.[25] Ruggli and Jensen were unable to separate a mixture of Auramine O and Malachite Green; these can be separated on paper using pyridine as solvent for adsorption and development, and subsequently exposing the paper to hydrochloric acid vapor. Chromatography of an ether or dioxane solution of the mixture after basification also separates Auramine O from Malachite Green.[39]

[45] The adsorption of direct dyes on fibrous cotton material by chromatographic technique has been mentioned by Flugel and Koch, *Textil-Rundschau,* **11,** 204 (1947); see also Lenoir, *Bull. soc. chim. France* (V) **9,** 475 (1942); Wykypiel, *Klepzig's Textil-Z.* **43,** 1034 (1939).

[45a] The acridine derivatives, Atebrin, Acriflavine and 5-aminoacridine hydrochloride, have been separated on paper from aqueous solution, using water or dilute hydrochloric acid for development; they were not separable by partition chromatography; Lederer, *Nature* **165,** 529 (1950).

The adsorption of azo dyes on paper generally runs parallel to the number of azo groups present; the more the number of azo groups, the stronger the adsorption.[39, 25] However, the affinity of the dye for cellulose and other factors play an important part. Thus a substantive monoazo dye (Direct Fast Yellow FF; a dehydrothiotoluidine derivative) is more strongly adsorbed than a nonsubstantive disazo dye (Cloth Fast Black B, an acid dye). Disazo dyes of the type ($A_1 \rightarrow Z \leftarrow A_2$) in which at least one of the two diazonium components, A_1 or A_2, contains a nitro group are weakly adsorbed; thus Naphthol Blue Black B (*p*-nitroaniline $\xrightarrow{\text{acid}}$ H-acid $\xleftarrow{\text{alk.}}$ aniline) is less strongly adsorbed than the monoazo acid dyes, Fast Red A and Orange II; the trisazo dye Chlorazol Green BNS (phenol $\leftarrow$ benzidine $\xrightarrow{\text{alk.}}$ H-acid $\xleftarrow{\text{acid}}$ *p*-nitroaniline) is less strongly adsorbed than the disazo dyes, Chlorazol Sky Blue FF and Benzopurpurine 4B. Neolan Red B (a chromium complex) is more weakly adsorbed than the parent azo dye, Eriochrome Red B. The solvent used for adsorption and development sometimes determines the order of separation; Benzopurpurine 4B is more strongly adsorbed than either Chlorazol Sky Blue FF or Durazol Fast Blue 8GS on filter paper using water as solvent, but the order is reversed when aqueous methyl cellosolve acetate is used.

Rutter has proposed a technique in which a narrow strip is cut from the edge to the center of a 11 cm. filter-paper disc; the strip is bent perpendicular to the disc and cut to a length of 1.5 cm.; the solution to be analysed is placed as a drop in the center of the disc, which is placed flat on a Petri dish with the strip dipping in the developing solvent contained in a small capsule. A glass plate, which may be engraved with a suitable scale to follow the course of development, is placed on the filter paper to retard evaporation.[46] Rutter has suggested the treatment of paper with 0.03% aqueous cetyl trimethyl ammonium bromide and drying; the paper thus acquires a net positive charge in contact with water, and is then more suitable for the chromatography of certain acid dyes.[46a]

Muller and Clegg have described a technique in which the preferential elution of a mixture of pigments is conducted in a restricted channel on filter paper; the progress of the elution is followed automatically as each fraction crosses a patch of monochromatic light.[47]

Brown[48] has described a method of adsorption separation on paper which he used for separating green leaf pigments from a carbon disulfide solution. A sheet of paper is placed between two glass plates (e.g. 6 inches square). The cover plate has a small hole (3/16 or 1/4 inch) at the center. A solution of the mixture is added dropwise through the hole, followed by the solvent; the components travel outwards in concentric zones, and clear separation of certain mixtures can be effected in this manner. Brown's technique can be applied to some vat dyes by vatting the dyestuff mixture with hydrosulfite and caustic soda and adding alcohol, dioxane, cellosolve or pyridine to the solution to stabilize the vat and reduce the affinity for cellulose. By the addition of an equal volume of pyridine to the aqueous caustic soda-hydrosulfite vat and by using a 1:1 mixture of water and pyridine containing caustic soda and hydrosulfite for development, the following mixtures have been separated; the dyes are mentioned in the order of increasing adsorbability: (1) Caledon Jade Green and dibenzanthrone; (2) Caledon Yellow 3G and dibenzanthrone; (3) Caledon Gold Orange G and Caledon Brilliant Purple 4R.[39]

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[46] *Nature* **161,** 435 (1948); *Analyst* **75,** 37 (1950). See also Clegg, *Anal. Chem.* **23,** 396 (1951); **22,** 48 (1950).

[46a] *Nature* **166,** 273 (1950).

[47] *Anal. Chem.* **21,** 1123 (1949).

[48] *Nature* **143,** 377 (1939).

A good separation of direct dyes can be obtained on cellulose acetate, nylon or vinyon fabric[39] after suitable activation, e.g. by treatment with *n*-butanol.[49] When two drops of an aqueous solution of the mixture are placed in the centre of the fabric, held taut in an embroidery ring, and a few drops of water are used for development, a clear separation of a mixture of Chrysophenine CH, Congo Red and Durazol Fast Blue 8GS is obtained.

Partition chromatography. The principle of partition chromatography was introduced by Martin and Synge[50] in their work on amino acids; instead of an equilibrium between a solid and a liquid phase as in the Tswett method, equilibrium is established between two liquid phases, one of the liquids being held in the form of a gel or in a suitable support. Silica gel, which absorbs water to the extent of about 70% while still remaining an apparently dry powder, was first employed. When a solution of the mixture under investigation in a water-immiscible solvent (e.g. chloroform) is passed through a column of silica gel, separations depending on the differences between the constituents in their partition coefficients can be effected. Filter paper sheets saturated with water were later used as the stationary phase;[51] phenol, *n*-butanol, collidine and certain other solvents partially miscible with water were the most satisfactory organic solvents. The individual amino acids were identified by means of color reactions or characterized by their R_F value, which is the ratio of the rate of movement of the band to the rate of movement of the advancing front of the solvent. The ratio of the distance travelled by a given substance to that travelled by a standard substance (e.g. proline as an amino acid standard, the ratio then being called the R_P value) can also be determined and used for identification. An important advance in partition chromatography on paper is the use of "two-dimensional" technique in which the mixture applied at one corner of a filter paper sheet is chromatographed in one direction with one solvent, and in a perpendicular direction with a second solvent.[51]

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[49] Cf. Boscott, *Nature* **159**, 342 (1947); Area Leao *et al.*, *Rev. brasil. biol.* **5**, 149 (1945).

[50] *Biochem. J.* **35**, 1358 (1941); Consden, *Nature* **162**, 359 (1948); for reviews, see *Biochem. J.* **43**, No. 4 (1948); Martin, *Annual Repts. Chem. Soc. London* **45**, 267 (1948); *Proc. Symposium on Partition Chromatography,* Biochem. Soc., London, 1949; *Annual Rev. Biochem.* **19**, 517 (1950). In connection with their work on the separation of amino acids on a starch column, Moore and Stein have described an automatic fraction collector; *Ann. N. Y. Acad. Sci.* **49**, 265 (1948). Rockland and Dunn propose the name "partography" for paper partition chromatography, and describe a device for accurate and rapid reading of R_F values; *Science* **111**, 332 (1950).

Sugars have been separated by filter paper partition chromatography; for identification, they are converted to furfurals by heating with acid and a color reaction with naphthoresorcinol is then used.[52] Other types of substances (among hundreds) which have been separated by this technique are alkaloids, porphyrins and pterins, penicillins,[53] natural and synthetic anthraquinone pigments,[53a] anthocyanidins,[53b] flavonol glycosides,[53c] alkylation products of 3,5-dinitroaniline,[53d] phenols and phenolic acids in connection with the bacterial oxidation of aromatic compounds,[53e] aliphatic acids, and inorganic compounds.[54] Phenolic acids are less strongly adsorbed in paper partition chromatography than the corresponding amides.[54a]

The effect of a substituent group on chromatographic behavior has been stated quantitatively as $R_M = \log\left(\frac{1}{R_F} - 1\right)$; ΔR_M is nearly constant for a group in similar molecules; when R_M is plotted against the number of substituent groups of any kind, a straight line is usually obtained. Irregularities are attributed to the effect of *ortho* and vicinal substituents.

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[51] Consden, Gordon and Martin, *Biochem. J.* **38,** 224 (1944); **40,** 580 (1946).

[52] Partridge and Westall, *Biochem. J.* **42,** 238 (1948).

[53] Goodall and Levi, *Nature* **158,** 675 (1946); Winston and Spark, *Science* **106,** 192 (1947).

[53a] Shibata, Takito and Tanaka, *JACS* **72,** 2789 (1950).

[53b] Spaeth and Rosenblatt, *Science* **110,** 258 (1949).

[53c] Gage and Wender, *Anal. Chem.* **22,** 708 (1950).

[53d] Roberts and Selby, *JCS* 2785 (**1949**).

[53e] Evans, Parr and Evans, *Nature* **164,** 674 (1949). See also Riley, *JACS* **72,** 5782 (1950).

[54] Linstead *et al., Nature* **162,** 691 (1948); **163,** 64 (1949).

[54a] Bray, Thorpe and White, *Biochem. J.* **46,** 271 (1950).

Values of R_F and R_M have been determined for several flavones, anthocyanins, catechins, and related compounds, as well as a series of benzene derivatives containing OH, OMe and COOH groups.[54b] In connection with work on chloramphenicol and its decomposition products, the R_F values for numerous aromatic nitro compounds, amines, aldehydes and carbinols have been determined.[54c]

Alumina-impregnated filter paper has been used for the separation of vitamin A and other Carr-Price chromogens from simple organic solvents.[54d] Filter paper treated with silicic acid effects separations (e.g. of the dinitrophenylhydrazones of methyl ethyl ketone, methyl *n*-propyl ketone and methyl isopropyl ketone) which are not possible on untreated paper.[54e]

Partition chromatography can be applied with advantage to the separation of dye intermediates and of the degradation products of dyes in connection with constitutional problems.

Ion-exchange chromatography. Ion-exchange is well known for its use in water softening and was first applied to the separation of inorganic anions and cations. Attempts to apply chromatographic theory to ion-exchange adsorption have been made more recently. Synthetic resins with selective adsorption and ion-exchange properties (Adams and Holmes, 1935) are now finding increasing use in the chromatographic analysis of ionizable organic compounds. Both acid resins for cation exchange and basic resins for anion change are available. Adsorption by these resins is largely determined by the charge carried by the solute (although exchange adsorption is a very complex process), and for elution an acid, alkali or salt is employed. Synthetic anion-exchange resins (e.g. Amberlite IR4) have been used for the chromatographic separation of amino acids (e.g. glutamic and aspartic acids in a wool hydrolyzate).[55] Other examples of the use of ion-exchange are nucleic acid analyses,[55a] adsorption of alkaloids,[55b] and isolation of the free sulfonic acids from azo dyes containing sodium sulfonate groups.[5a] Richardson has observed that the dye acids of Sky Blue FF and other dyes of large molecular size are rapidly adsorbed by the ion-exchange resin Deacidite B to a low final equilibrium figure; with a decrease in the molecular size a point is reached at which a slow diffusion into the structure of the resin begins.[13g, 55c]

[54b] Bate-Smith *et al.*, *Biochim. et Biophys. Acta* **4,** 427, 441 (1950).

[54c] Smith and Worrel, *Arch. Biochem.* **28,** 1 (1950).

[54d] Datta *et al.*, *Nature* **164,** 673 (1949).

[54e] Kirchner and Keller, *JACS* **72,** 1867 (1950).

[55] Consden, Gordon and Martin, *Biochem. J.* **42,** 443 (1948).

[55a] Cohn, *JACS* **72,** 1471 (1950); *et sequa.*

[55b] Mukherjee, Gupta and Bhattacharya, *J. Indian Chem. Soc.* **27,** 156 (1950).

[55c] See also *JCS* 910 (**1951**).

Ion-exchange chromatography can be used for the separation, purification and analysis of ionizable dyes (acid and direct cotton dyes containing sulfonic groups as well as basic dyes containing "onium" groups), and in the identification and analysis of the products obtained by reductive fission of azo dyes. Cotton fabrics may be chemically modified so that they function as anion- or cation-exchangers, and may then prove useful in the ion-exchange chromatography of dyes.[55d] It should be possible also to use a protein as the adsorbent, and obtain data on the "exchange affinity" of dyes, which may assist an understanding of the relation between the constitution of dyes and their affinity for protein fibers.

The adsorption of a surface-active or water-insoluble acid (e.g. a fatty acid or lecithin) on alumina, activated charcoal or other adsorbent, as a "primary adsorbate," enables cations or bases (e.g. 5-aminoacridine) to be adsorbed as "secondary adsorbates" which can then be eluted by acid solution; conversely cationic surface-active agents can be used for preparing adsorbents for acids or anions.[56]

An example of "chemichromatography" is the use of a column of a mixture of starch and 8-hydroxyquinoline for the separation of inorganic ions and for the quantitative estimation of variations in zinc content of a cupro-nickel-zinc alloy.[56a] The use of mordant dyes for similar purposes and, conversely, the use of copper, chromium and other salts capable of forming metal-dye complexes for the separation of mordant dyes are possible applications of chemichromatography.

THE GREEN-CLAYTON SCHEME OF IDENTIFICATION

Witt in 1886 prepared a scheme of analysis based on the shade, solubility and behavior towards caustic soda, by which the small number of dyes then known could be classified into groups. A year later Weingartner suggested the use of two reactions for further subdivision: precipitation by tannin which distinguished basic from acid colors, and reduction with zinc dust. In 1893, A. G. Green evolved a procedure which has stood the test of time and which is so comprehensive that the numerous new dyes discovered since then can be fitted into the scheme with suitable modifications.[2] The scheme is dependent on two principles. The first is division into the following four groups on the basis of solubility and dyeing properties: (1) basic dyes, soluble in water and dyeing tannin-mordanted cotton; (2) "salt dyes" (direct cotton dyes), soluble in water, not precipitated by tannin and dyeing unmordanted cotton; (3) acid and acid-mordant dyes, soluble in water, not precipitated by tannin and without affinity for unmordanted cotton; (4) water-insoluble dyes (sulfide, mordant, vat dyes, etc.). The second principle is the behavior of the dyes on reduction and reoxidation as indicated in Table I.

[55d] Hoffpauir and Guthrie, *Textile Research J.* **20,** 618 (1950).

[56] Weiss, *Nature* **162,** 372 (1948).

[56a] Robinson in Ref. 13*g*; see also Erlenmeyer and Dahn, *Helv. Chim. Acta* **22,** 1369 (1939).

Green thus constructed a series of twenty-seven tables with the aid of which a single dyestuff in commercial use can generally be classified without difficulty. The shade of the dye applied to a suitable textile fiber is an important clue to its identity. After determining the dyeing class, the dyestuff is taken up on a small hank of yarn and the shade compared with the shades in a manufacturer's shade card for the relevant class of dyestuff. Green's and other tables for dyestuff analysis are therefore arranged according to the shades.

TABLE I

Decolorized by zinc dust				
Color restored on exposure to air	*Color not restored by air, but by other oxidizing agents*	*Color not restored by air, or other oxidizing agents*	*Unaffected or decolorized slowly and partially by zinc dust*	*Not decolorized by zinc dust, but changed in shade*
Azines Oxazines Thiazines Acridines Phthaleins (violet and blue) Indigoids	Triphenylmethanes Phthaleins (red)	Nitro Nitroso Azo	Quinolines Thiazoles	Anthraquinones

A preliminary scheme of analysis is outlined in Tables II and III. Dyestuffs are first classified on the basis of their solubility in water and of their dyeing properties, using standard procedures for the dye-trials.[57] Soluble dyes are thus divided into seven groups: (1) Direct cotton dyes; (2) Acid and acid-mordant dyes, the latter class being distinguished by dyeing on chromed wool and noting that little or no color is stripped on treating the pattern with boiling 2% ammonia; (3) Metallized dyes of the Neolan and Palatine Fast types; (4) Basic dyes; (5) Some sulfur dyes containing sodium sulfide, confirmed by testing for sulfur by boiling with stannous chloride and hydrochloric acid and observing the brown or black stain produced on lead acetate paper; (6) Solubilized vat dyes of the

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[57] See Chapter VI.

Indigosol and Soledon types, the precipitated vat dye obtained by treatment of the aqueous solution with dilute sulfuric acid and sodium dichromate being then examined; (7) Cellulose acetate dyes of the Solacet type; these dye wool and are hydrolyzed to an insoluble azo or anthraquinone dye and sulfuric acid on boiling with concentrated hydrochloric acid. The next stage is to study the behavior of an aqueous solution of the dyestuff at room temperature and at 60° on the addition of (a) hydrosulfite, and (b) 5% caustic soda solution followed by hydrosulfite; if decolorization takes place, a drop of the solution is placed on filter paper and the behavior on (a) exposure to air and (b) treatment with a drop of an aqueous solution containing 2% potassium persulfate and 2% sulfuric acid is observed. The typical behavior of the dyestuffs of various chemical classes is shown in Table II, in which D = decolorized, CR = color restored, CNR = color not restored, PD = partially or difficultly decolorized, ND = not decolorized, and DZn = decolorized by boiling with glacial acetic acid and zinc dust. The Table refers only to the qualitative behavior of each class of dyestuff, and the precise color changes must be carefully observed and compared with those of authentic samples of the suspected dyestuffs.

Insoluble dyestuffs may first be classified as in Table III, and the specific dyestuff identified by the colorations produced by such reagents as (a) alkaline hydrosulfite, (b) sodium sulfoxylate-formaldehyde acidified with acetic acid, (c) concentrated sulfuric acid, (d) concentrated nitric acid, and (e) warm concentrated sulfuric acid and boric acid.[58] Vat and sulfur dyes are applied to cotton and the tests carried out on the dyed fiber. Lakes of direct, acid, acid-mordant and basic dyes are decomposed by boiling with 5% sodium carbonate solution; some lakes of basic dyes may require boiling 5% caustic soda solution saturated with salt. The solutions are then examined as in Table II for identifying the chemical class. By precipitation of the solutions with barium chloride the tungstic, molybdic and other acids used for laking may be separated and analysed. Azoics can be crystallized from organic solvents (e.g. dioxane) and characterized by their melting points.[59]

When the chemical and dyeing class to which a dye belongs has been found, the shade, characteristic color reactions and other simple specific tests[60] are often adequate for identifying a commercial dye of known constitution, especially when an authentic sample is available for com-

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[58] For further details and refs. regarding the identification of vat dyes, see Chapter XXX.

[59] For the identification and analysis of azoic coupling components and the Rapid Fast and Rapidogen types of printing colors, see Chapter XXII.

[60] See CI and ST.

TABLE II

SOLUBLE DYES

Chemical class	(1) *Neutral hydrosulfite*	(2) *Alkaline hydrosulfite*	(3) *Expose (2) to air*	(4) *Acid persulfate on (2)*	(5) *Special tests*
Nitro	D	D	CNR	CNR	
Nitroso	D	D	CNR	CNR	Test for iron (Naphthol Green B)
Azo	D	D	CNR	CNR	Test for chromium and copper; bleeding tests; color reactions.
Thiazole	ND or PD	ND or PD			Test for Primuline and Thioflavine.
Diphenylmethane (Auramine)	ND or slightly	ND or slightly		CR	
Triphenylmethane					
(a) Amines (b) Phenols	PD	D	CR in some cases	CR	DZn. Acid triphenylmethane dyes are decolorized by neutral hydrosulfite; after decolorization with alkaline hydrosulfite the color returns only with acid persulfate.
Xanthenes					
(a) Pyronines	PD	D	CR in some cases	CR	
(b) Phthaleins	ND or PD	D	CR	CR	DZn. If ether extraction of (4) gives a colored solution, an acid dye.
Acridine	ND	Yellow precipitate			
Azine	Yellow	Decolorized	CR	CR	
Oxazine	D	D	CR	CR or changed to brown	

TABLE II (*Continued*)

Chemical class	*(1)* *Neutral hydrosulfite*	*(2)* *Alkaline hydrosulfite*	*(3)* *Expose (2) to air*	*(4)* *Acid persulfate on (2)*	*(5)* *Special tests*
Dioxazine (Sirius Supra Blue type)	D	D	CR	CR	
Thiazine	D	D	CR	CR or changed	Basic mordant dyes of the oxazine and thiazine classes (e.g. Modern Violets, Brilliant Alizarin Blues) are distinguished by their being precipitated from aqueous solution by chromium trifluoride.
Anthraquinone:					
(a) Acid dyes	ND, but changed in shade		CR	CR	
(b) Cellulose acetate dyes (Solacet type)	ND, but changed in shade				Boil with hydrochloric acid; test filtrate for sulfuric acid and precipitate for an aminoanthraquinone.
(c) Solubilized vat dyes	ND, but changed in shade		Colored precipitate		Analyze precipitate as for vat dyes.
Indigoid					
(a) Acid dyes	Yellow solution		CR	CR	
(b) Solubilized vat dyes	Yellow solution		Colored precipitate		Analyze precipitate as for vat dyes.
Phthalocyanine					
(a) Sulfonic acids	Purple	Purple	CR	Green	
(b) Basic dyes	Bluish green precipitate				
Cyanine	ND	D	CR	CR	DZn
Quinoline (Quinoline Yellow)	ND	ND; yellow precipitate			

TABLE III
Dyestuffs Insoluble in Water

	(1)	(2)	(3)	(4)
Class of dyestuff	*Alkaline hydrosulfite*	*Acid persulfate added to (1)*	*Boiling 5% sodium carbonate solution*	*Boiling 95% alcohol*
Nitro pigments	Decolorized	CNR	Characteristic coloration with strong alkali	Some soluble
Cellulose acetate dyes				
Anthraquinone derivatives	Soluble with change in color	CR	Insoluble	Soluble
Azo compounds	Decolorized	CNR	Insoluble	Soluble
Phthaleins	Decolorized	CR	Soluble	Soluble
Sulfur	Yellow or brownish yellow solution which dyes cotton	CR	Insoluble	Insoluble
Sulfurized vat	Yellow or brownish yellow solution which dyes cotton	CR	Insoluble	Insoluble
Indigoid	Yellow, brown or orange solution which dyes cotton	CR	Insoluble	Insoluble
Anthraquinonoid vat	Deeply colored solution which dyes cotton	CR	Insoluble	Insoluble
Mordant				
Anthraquinone derivatives (Alizarin)	Red-brown solution which does not dye cotton	CR	Soluble	Soluble

TABLE III (*Continued*)

Class of dyestuff	(1) *Alkaline hydrosulfite*	(2) *Acid persulfate added to (1)*	(3) *Boiling 5% sodium carbonate solution*	(4) *Boiling 95% alcohol*
Nitrosophenols	Decolorized	CNR	Soluble	Soluble
Phthaleins	Decolorized	CR	Soluble	Some soluble
Oxazines	Decolorized	CR	Soluble	Some soluble
Azoic	Decolorized	CNR	Insoluble	Some soluble
Lakes of mordant dyes (Turkey Red type)	Colored solution	Colored (not necessarily original color)	Insoluble	Insoluble
Lakes of direct, acid and acid-mordant dyes	Decolorized	CNR	Color dissolves; solution dyes cotton or wool by usual methods.	
Lakes of basic dyes			Lake decomposed; solution of base in acetic acid dyes tannin-mordanted cotton.	
Indulines and Nigrosines	Insoluble		Insoluble	Some soluble
Phthalocyanines	Insoluble		Insoluble	Insoluble
Quinoline Yellow	Unchanged		Insoluble	Soluble

parison. Spot tests,[61] such as the acid and alkali colorations, are conveniently carried out in a porcelain plate provided with a series of hollows for this purpose. Characteristic tests for some dyes may be mentioned. (1) Many azo dyes give characteristic colors in concentrated sulfuric acid. Azo dyes are partly or completely decolorized by bromine water and one of the products for each dye is usually the diazonium bromide of the primary component; by coupling with β-naphthol and observing the characteristic color reactions of the new dye the original dye may often be identified.[8] (2) The color of the hydrosulfite-alkali vat, the acid vat, the sulfuric acid solution and the nitric acid solution, and the color changes when the dyed yarn is treated with oxidizing agents, are useful for anthraquinonoid vat dyes. A scheme of dyestuff analysis specially concerned with vat and azoic colors has been largely based on the behavior of the dyes towards aqueous and concentrated pyridine.[62] (3) Some of the mordant colors, such as Alizarin, are polygenetic, and by immersing in a boiling aqueous solution or suspension of the dye a piece of calico printed in narrow stripes of aluminum, iron, chromium, nickel, cobalt, titanium, tin, antimony and copper ("Scheurer Streifen"), a characteristic "spectrum" is obtained. (4) Aniline Black turns brown with hypochlorite solution and is decolorized by strong permanganate solution. (5) Methylene Blue turns green with nitric acid. (6) The phthalein dyes exhibit characteristic color changes and fluorescences with change in pH.

Formanek and Knop[63] have determined the absorption maxima of a large number of commercial dyes, and those possessing characteristic absorption bands, such as the triphenylmethanes, azines, oxazines and thiazines, can be thus identified. Many hydroxyanthraquinones, azophenols and hydroxyketonic dyes give with concentrated sulfuric acid and boric acid beautifully colored solutions with characteristic absorption spectra.[63, 64] The Hardy Recording Photoelectric Spectrophotometer (General Electric Co.) is a valuable and versatile instrument which can be used for obtaining both transmission curves for dyestuffs in solution and reflection curves for dyed fabrics or colored surfaces, for qualitative and quantitative analysis, and for shade matching purposes.[65] Metallic constituents or impurities can be detected and estimated by examining the arc spectrum produced by the dyestuff placed in the hollow tip of an electrode; the dyestuff may be ashed first and mixed with a salt of predetermined spectral character.[66] X-Ray patterns were used by IG for the identification of crystalline substances, and the method was found to be particularly useful for identifying members of the Naphtol AS series in mixtures.[67]

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[61] For an account of the technique of spot tests in general, see Feigl, Spot Tests, Nordemann, New York, 1937.

[62] Zühlke, *Melliand Textilber.* **17,** 866 (1936).

[63] Untersuchung und Nachweis org. Farbstoffe auf Spektroskopichem Wege, 2nd ed., Springer, Berlin, 1926.

[64] Fierz-David and Yarsley *in* Allen's Commercial Organic Analysis, Vol. VI, 5th ed., Churchill, London, 1933.

[65] For examples, see Selling, *J. Soc. Dyers Colourists* **63,** 419 (1947); Mersereau and Barach, *Textile Research J.* **18,** 436 (1948).

Vesce[68] has described a microcrystallization technique for the identification of dyestuffs. The dyestuff is dissolved in concentrated sulfuric acid, allowed to stand, and then examined under the microscope for the characteristics of the deposited crystals. The method is valuable for azo dyes and lakes. Microscopic examination and photographic records of pigments in aqueous suspension and of the intermediates undergoing diazotization and other reactions during manufacture provide useful data for the identification of pigments and for the control of manufacturing processes.[69] Microscopy, employing light and electron microscopes, is useful also for particle size determinations.[70]

For the precise identification of a dye a more elaborate chemical investigation involving degradation and other experiments may become necessary; this is true for instance of azo dyes because of their very large number and the minor variations in structure and properties among the dyes prepared by permutations and combinations of a relatively small number of intermediates. Reductive fission and characterization of the products is the essential procedure for the identification of an azo dye (see Chapter XI).

The identification of dyes on the fiber is based on the same general principles as their identification in substance. The procedures in the two cases are in fact interdependent. Dye-fiber relationships constitute one of the essential clues in dyestuff detection, and further, a convenient method for the isolation of a coloring matter free from inorganic and nontinctorial diluents is to dye it on a suitable fiber; color reactions and spot tests are often best carried out on the dyed fiber. Conversely, a dyed or printed textile may have to be stripped (e.g. by solvent extraction) and the dye then examined in substance; the solvent extract may be directly used for observing the absorption spectrum. There are, however, a few special problems associated with the identification of dyestuffs on the fiber. While dyestuffs in substance would normally be available in quantities sufficient for a comprehensive analysis, a sample of a dyed or printed fabric a few inches square may be all that is available, so that micro technique and skill of a high order, combined with an extensive knowledge of the dyeing and printing industries and trades, are called for. The identification of the fiber or mixture of fibers[57] in the colored textile must be the first step, since it narrows down the search for the dyestuff. The dyestuffs commonly encountered are acid and acid-mordant dyes on wool; acid and direct cotton dyes on silk; substantive, azoic, vat and sulfide dyes on cotton (with the addition of chrome-mordant and basic dyes in calico prints), and the same classes with the exception of the sulfide dyes on viscose and cuprammonium rayons; and a distinct group of azo and anthraquinone dyes on cellulose acetate. Mixed fibers present additional problems except when the warp and weft are of two different fibers so that they can be pulled out and examined separately. Water-proof and other finishing materials frequently interfere with the identification of dyestuffs, a common effect being to slow down the chemical reactions (e.g. the reduction of an azo dye by hydrosulfite) in the tests; the finishing materials must therefore be carefully removed as far as possible.

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[66] Sawyer, Experimental Spectroscopy, Prentice-Hall, New York, 1944.

[67] *FIAT* **1313, III.** See also Susich, *Anal. Chem.* **22,** 425 (1950).

[68] Mattiello's Protective and Decorative Coatings, Vol. II, p. 124, Wiley, New York, 1942.

[69] Pratt, The Chemistry and Physics of Organic Pigments, Wiley, New York, 1947.

[70] Brubaker, *Ind. Eng. Chem. Anal. Ed.* **17,** 184 (1945).

A mixture of dyes may be present in a dyeing for several reasons. The dyeing may have been carried out by a commercial dyestuff which is itself a mixture of dyes or by a mixture of dyes used by the dyer in order to produce a given shade. The shade obtained from one dyestuff may be "topped" by using a small amount of a second dyestuff, which may belong to the same or a different chemical and dyeing class. Topping may be for the purpose of shade matching or for improving brightness and fastness. In dyeing indigo on wool it is common practice to "bottom" with logwood or "top" with an acid or acid-mordant color; a red color (changing to violet by the addition of stannous chloride) is produced by boiling with dilute hydrochloric acid if logwood is present. Materials which have been dyed in unlevel shades may be redyed brown or black, sometimes after partial stripping. The identification of the dyestuffs in a compound shade on a fiber thus involves problems somewhat different from those discussed in connection with dyestuffs in substance. A mixture of dyes of different chemical classes is relatively easy to spot by the use of specific reagents; a mixture of two acid dyes, one of the azo and the other of the anthraquinone class, can for instance be detected by the behavior towards reduction and reoxidation. If it is possible to strip the shade partially or completely by treatment with water, weak alkali, dilute acetic acid or organic solvents, the solution can then be examined by the methods described earlier. Vat dyes on cellulose can be isolated by dissolving the dyed fiber in concentrated sulfuric acid and precipitating the vat dye by dilution with water; and it may be possible to separate the dyes in a mixed dyeing at this stage by fractional precipitation. When the dyeing consists of a mixture of dyes of different types, solvent extraction might effect a separation; for instance, indigo can be extracted with a mixture of phenol and solvent naphtha from a dyeing in which the vat dye and an acid or chrome dye are present.

Clayton in 1937 described a scheme for the identification of dyestuffs on the fiber.[71] While it is based, as indeed any procedure for dyestuff analysis must be, on Green's tables, new and more effective reagents have been used, the dyes discovered in the interval have been taken into account, and as a result Clayton's tables are substantially different from Green's. The Clayton tables represent the most satisfactory scheme we now have for identifying dyestuffs. Although they refer to dyestuffs on the fiber, it is obvious that they can also be used successfully for the examination of dyestuffs in substance. The following reagents are used: (1) dilute ammonia (1 cc. ammonia, 0.880 sp. gr., in 100 cc. water); (2) 5% caustic soda solution; (3) 5% sodium carbonate solution; (4) 5% ammonium chloride solution; (5) 3% hydrogen peroxide; (6) vat dye developer (8 g. ammonium chloride and 1 g. ammonium persulfate dissolved in 100 cc. cold water); (7) Formosul G (20 g. Formosul are dissolved in 75 cc. hot water and diluted with 75 cc. cold water and 50 g. ethylene glycol); (8) ethylenediamine (the commercial product is colorless, has sp. gr. 0.97 and b.p. 117°; it is readily soluble in water and contains 60–70% of base); and (9) Developer O (1 g. ammonium persulfate and 0.5 g. ammonium dihydrogen phosphate dissolved in 100 cc. water).

The first two experiments are (1) a simple stripping test; and (2) the behavior of the pattern towards Formosul G, and of the treated pattern towards air or 3% hydrogen peroxide. The stripping test can give information which immediately indicates the dyeing class; thus if dyed wool stains white cotton when the two are boiled together in 5% sodium carbonate solution for a minute, a direct cotton dye is indicated. The action of ethylenediamine is a valuable test for many dyes; since commercial ethylenediamine is a powerful solvent for dyes, is strongly basic and has reducing properties. Indigoid dyes are converted into their leuco compounds on warming with this solvent at 50–60° or even at room temperature; most anthraquinone dyes on the fiber are only slightly reduced, but they dissolve in the boiling solvent, either directly or as the leuco derivatives. From the color of the solution and of the fiber, together with the behavior of both in the reoxidation tests, the dyeing and chemical class, as well as some of the dyes specifically, can be identiied. All vat dyeings and prints give solutions of the leuco compounds vhen they are treated with ethylenediamine to which a little glucose and a few drops of 50°Tw. caustic soda solution are added. *n*-Butylamine is also an effective solvent in conjunction with hydrosulfite for stripping vat dyes.[8] Some Neolan colors and chromium lakes of acid-mordant azo dyes are difficult to reduce on the fiber with Formosul G, even after a preliminary boil with 16–30% hydrochloric acid; but on warming with ethylenediamine the metal-dye complex dissolves without alteration in color, and the solution is rapidly decolorized by reduction when a little hydrosulfite is added. Azoic dyes are extracted by ethylenediamine, and the solution is quickly and irreversibly decolorized by the addition of hydrosulfite. In using ethylenediamine for wool and silk patterns, the degradative action of the basic solvent on the protein fibers has to be borne in mind, but the dyes dissolve much more rapidly. While most substantive dyes on cotton and viscose bleed on treatment with boiling 5% caustic soda solution for a minute, the fast to light dioxazine blues, such as Sirius Supra Blue FFRL, are resistant; but they are stripped completely by cold ethylenediamine in a few minutes. Sulfur dyes on cotton are characterized by the liberation of hydrogen sulfide (lead acetate paper test) on warming with zinc or stannous chloride and hydrochloric acid, combined with the ready decolorization effected by boiling 3°Tw. sodium hypochlorite solution. The Indocarbon type is not decolorized by hypochlorite, and is identified by the reddish solution it gives in boiling ethylenediamine, which reverts to black on dilution with tap water containing dissolved oxygen. Sulfur Black dyeings give greenish solutions in ethylenediamine.

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[71] *J. Soc. Dyers Colourists* **53**, 178 (1937); see also Bradley and Derrett-Smith, *ibid.* **56**, 113 (1940); Redston, *Can. Textile J.* **55**, No. 6, 34 (1938).

Whittaker and Wilcock[72] have described tests for the identification of dyestuffs on the fiber which they have found useful for routine work, and some examples may be quoted. Chlorazol Fast Orange AGS dyeings, when placed in alkaline hydrosulfite solution, change in color to a red-violet shade, but can be ultimately stripped to a white. Direct and developed dyes may be distinguished by placing them between two layers of bleached calico, wetting with water and drying with a hot iron; the direct dyeings stain the calico much more than the developed dyeings. Aniline Black gives a green solution when the pattern is treated with just sufficient concentrated sulfuric acid to char the fiber, and then with cold water. Azoics are detected by stripping with alkaline hydrosulfite in presence of undyed viscose and observing the ultraviolet fluorescence of the viscose as well as the stripping liquor. Many azoics are soluble in chloroform and other organic solvents. Basic dyes on a tannin mordant become very flat because of the formation of blue-black iron tannate, when the pattern is warmed with ferric chloride solution and washed. Turkey Red dyeings change to a maroon on boiling with titanous chloride solution; and the characteristic violet color of sodium alizarinate is obtained when the pattern is distintegrated with concentrated sulfuric acid and then carefully treated with strong caustic soda solution. Carbon Black is the main black used for the mass pigmentation of rayon, and is detected by its stability towards the reagents mentioned earlier. Blacks on wool which are fast to potting are distinguished by their not being destroyed when the pattern is boiled for two minutes with 2% nitric acid. Logwood Black gives a red color, changed to violet with ammonia, when the pattern is boiled with dilute acid. Indigo gives a bright yellow spot with a green rim when the pattern is spotted with concentrated nitric acid; indigo can be sublimed off the fiber by gently heating the pattern in a test tube. Dispersed dyes on cellulose acetate are distinguished from the Solacet type by the fact that the former are completely stripped by treatment with a mixture of methylene chloride and benzene (40:60).

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[72] Whittaker and Wilcock, Dyeing with Coal-tar Dyestuffs, 5th ed., Baillière, Tindall, and Cox, London, 1949.

Metals present in dyed and printed materials provide data regarding the nature of the dyestuffs. The metals, however, may not be associated with the dyestuffs, but with rot-proofing, water-proofing, delustering and weighting processes; in addition the natural fibers contain small amounts of mineral matter which may persist in the finished textiles. The detection and estimation of metals in fibers are carried out after ashing the sample in a platinum crucible. In dealing with small samples, spot tests and micro technique using organic reagents are advantageous.

Detailed procedures for the detection of metals in fibers, dyes and pigments have been described by Clayton.[73] Since the chromium colors are largely used for wool, the identification of chromium on wool still leaves a wide field for search to specify the dyestuff present. Except for mineral khaki and substantive dyes aftertreated with potassium dichromate or chromium fluoride, chromium is not likely to be found in dyed cotton, but only in prints; and when chromium is detected in a printed pattern of cotton or viscose, the dyestuff must belong to a small group of acid-mordant dyes applicable in conjunction with a chromium salt such as the fluoride or the acetate. A black on cotton containing copper and chromium points to Aniline Black; and aluminum and calcium in a bright red dyeing or print indicate Turkey Red.

An extract of the pattern may be used for determining the absorption spectra. Fluorescence under ultraviolet light sometimes gives useful indications, e.g. of β-naphthol and thiazole derivatives.[74]

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[73] *J. Soc. Dyers Colourists* **53**, 380 (1937).

[74] Fierz-David, *J. Soc. Dyers Colourists* **45**, 133 (1929).

Furs are usually dyed by the oxidation of *p*-phenylenediamine, aminophenol or *o*-aminophenol on the fiber; the first is the most imporit, being largely used for black shades. Dermatitis may be caused by ed fur, and the analysis of fur dyes from this point of view has been restigated by Cox.[75] The color reactions of such intermediates and es have been tabulated by Schulze.[76]

Analysis of organic pigments.[77] The general scheme for the analysis dyestuffs in substance may be used with the modifications necessary cause of the insolubility of the pigments in water. The main classes organic pigments are nitro compounds; azoics; lakes of acid, basic and ordant dyes; vat dyes; and phthalocyanines. They are identified as dicated in Table III. Acid dyes are extracted from the lakes by boiling dium carbonate solution, and basic dyes by boiling caustic soda solution turated with salt; the dye after acidification with acetic or formic acid transferred to wool. Lakes of mordant dyes such as Alizarin can ually be decomposed by boiling with caustic soda solution and the ordant dye isolated by acidification. Madder lakes can also be decomosed by boiling with 6N hydrochloric acid.[78]

Common pigments of known constitution, a series of which have been bulated, can be identified by their appearance, dry and when wetted y sulfuric acid, viewed by daylight and ultraviolet light; but there are fficulties due to the presence of impurities.[79] Carbon Black and Aniline lack in admixture may be differentiated by removal of the latter as a rown oxidation product by treatment with nitric acid.[80]

EVALUATION OF DYESTUFFS

Three types of methods are available for evaluating dyestuffs: (1) emical analysis; (2) colorimetric estimation; and (3) examination of e dyeing properties or "dye-trials."

Chemical analysis. The estimation of a dye by chemical analysis is ossible when the constitution is known and when the dye possesses a active group amenable to reduction, oxidation or other chemical reacon in a quantitative manner. The most widely applicable method is duction by titanous chloride;[81] the titration may be carried out directly, the dye may be reduced by excess of the reagent which is then deter-

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Analyst **54,** 694 (1929); **58,** 738, 743 (1933); **59,** 3 (1934).

Mitt. Textilforsch-Anstalt Krefeld **9,** 27 (1933); see also Griebel and Weiss, *Z. Untersuch. Lebensm.* **67,** 86 (1934).

Green, *J. Oil & Color Chemists' Assoc.* **11,** 38 (1928).

Bainbridge, *J. Assoc. Offic. Agr. Chemists* **25,** 956 (1942).

Barker and Walker, *J. Oil & Color Chemists' Assoc.* **23,** 19 (1940).

Anon, *Farben Ztg.* **47,** 189 (1942).

Knecht and Hibbert, New Reduction Methods in Volumetric Analysis, 2nd ed., Longmans, London, 1925.

mined by back titration. The titanous chloride solution is made up by boiling 50 cc. of the commercially available 20% solution with 100 cc. concentrated hydrochloric acid for a minute, cooling and making up to 2 liters in a storage bottle, which is connected to a burette and a hydrogen generator in such a manner that air may be replaced by hydrogen in the entire apparatus and the solution in the burette and the storage bottle preserved in an atmosphere of hydrogen. Exposure of the solution to sunlight must be avoided since titanous chloride is liable to photochemical oxidation with formation of titanic chloride; but slow decomposition is unavoidable and titanous chloride must be standardized immediately before use. This is carried out by titrating against standard ferric alum solution with ammonium sulfocyanide (or Methylene Blue in presence of salicylic acid) as indicator. Titanous sulfate has been stated to have advantages over the chloride.[82] Nitro compounds can only be estimated by the indirect method, while some azo (e.g. yellow) dyes are preferably estimated in this manner; boiling for about ten minutes with excess of the reagent in a current of carbon dioxide completes the reduction and the excess is then determined by cooling and titrating with ferric alum. Azo dyes not precipitated by hydrochloric acid can be estimated directly, the dye acting as its own indicator; many azo dyes precipitated by hydrochloric acid can also be estimated directly in presence of Rochelle salt. Nitroso compounds and the quinones soluble in water, alcohol, acetic acid and other water-miscible solvents can be titrated directly with titanous chloride. Acid and basic dyes (e.g. Safranine, Methylene Blue, Malachite Green, Magenta, Rhodamine, Gallein, Acid Magenta) which give colorless or pale yellow leuco compounds can be titrated directly; addition of alcohol is sometimes useful for preventing turbidity during the titration (e.g. for Eosine A and Rhodamine). Indigo and other indigoid dyes can be estimated by heating with concentrated sulfuric acid to effect sulfonation, and titrating an aqueous solution of the sulfonic acid in presence of sodium tartrate. By boiling Alizarin in alcoholic solution with excess of titanous chloride in presence of·Rochelle salt, an intense blue-green solution is obtained, the color being due apparently to the reduction of Alizarin to 1,2-dihydroxy-9-anthranol which forms a blue-green complex with titanous chloride; the color is destroyed when the titanous salt is used up by titration with ferric alum, so that the excess of titanous chloride (over the equivalent of four atoms of hydrogen required for reducing the Alizarin) is thus obtained. Alizarin S, Anthrapurpurin and Flavopurpurin can be estimated similarly, but with

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[82] Callan and Henderson, *J. Soc. Chem. Ind.* **41,** 158 (1922). Shaposhnikov and Geizer, *Anilinokrasochnaya Prom.* **3,** 445 (1933), consider that the titanous chloride method for determining azo dyes is unreliable and inconvenient.

-nitroalizarin (Alizarin Orange) the reduction stops at the stage of the minoalizarin.[81]

Rawson in 1888 suggested a method of estimating the acid dye aphthol Yellow S by titration with the basic dye Nile Blue, depending n the two forming an insoluble complex. The mutual precipitation of cid and basic dyes has since been investigated by other workers. Brown nd Jordan,[83] working with 0.2% dyestuff solutions and noting the end oint by the appearance (spot on filter paper) of a ring of the color of the recipitating solution, evaluated Auramine O, Safranine* and Magenta* gainst Indigo Carmine; Brilliant Green* and Malachite Green* against range II or Eosine; Methyl Violet against Naphthol Yellow S; Methylne Blue* against Crystal Scarlet; and Victoria Blue against Tartrazine. or the starred dyes an addition of tannic acid and sodium acetate are ecessary. Anionic and cationic detergents have been estimated by itration with dyes, the colored ions of which are of opposite sign, in he presence of a non-miscible solvent for the dye-detergent complex; onversely, the procedure should be applicable for the estimation of basic, cid and direct cotton dyes.[83a]

Basic dyes can be determined by precipitating them from acid olution by means of phospho- or silico-tungstic acid and igniting the recipitate.[84]

Dyes containing nitrogen, sulfur or a halogen can be estimated in erms of these elements, provided they are not present in the impurities ssociated with the dye; estimation of nitrogen has thus been used for etermining the quantity of an azoic dye on the fiber. Methods for the stimation of indigo, azoic coupling components, solubilized vat dyes. nd other dyes by special methods have been mentioned elsewhere.

Colorimetry. The colorimetric estimation of dyestuffs is generally impler and more rapid than chemical analysis, and is widely employed. he absorption curve completely specifies the color in terms of wave ength and intensity,[85] but for practical purposes colorimeters are

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[3] *J. Soc. Dyers Colourists* **39,** 203 (1923); the earlier work is reviewed in this paper; see also Ruggli and Fischli, *Helv. Chim. Acta* **7,** 507 (1923).

[3a] Barr *et al., J. Soc. Chem. Ind.* **67,** 45 (1948). According to Ref. 5a the titration of acid dyes with Fixanol has been used technically for estimating the concentration of dyebaths used for dyeing anodized aluminum.

[4] Kozlov, *J. Applied Chem. U.S.S.R.* **9,** 558 (1936); Payne, *J. Soc. Dyers Colourists* **50,** 320 (1934).

[5] See Chapter VII. Standard absorption curves of pure samples of many commercially important dyes have been determined by the U.S. Bureau of Standards; Gibson *et al., Sci. Papers Bur. Standards* No. 440, 18, 121 (1922); Appel and Brode, *Ind. Eng. Chem.* **16,** 797 (1924); Appel, Brode and Welch, *ibid.* **18,** 627 (1926); Brode, *ibid.* 708. The cited papers describe methods for the spectro-

employed in which the color of the solution under test is compared with the color of a standard solution of the same dye. The two solutions are placed in two tubes supported side by side. Light passes up the tubes and illuminates the two halves of an eyepiece field. White light may be used, but for more accurate results, especially with weakly colored solutions, light of a narrow range of wave length (obtained by means of suitable color filters), corresponding to the main absorption band of the dye, is employed. The two halves are equalized by altering the depths of the solutions by means of the movable plunger with which each tube is fitted. The concentrations of the solutions are then inversely proportional to the depths, provided Beer's law (the molar extinction coefficient being independent of the concentration) is obeyed.[86] Instead of using two solutions (unknown and standard), the light transmitted by the solution under test may be matched in the eyepiece field by an optical system in which the components of a beam of light can be varied. In the Leitz colorimeter the solution under test is viewed through filters and matched against a standard neutral gray solution. By such methods the need for a standard solution of the dye is eliminated. Instead of visual matching, photoelectric devices can be employed.[87, 88]

Colorimetric methods for the estimation of dyes in dyebaths have been discussed recently by Vickerstaff.[5a] For water-soluble dyes it is necessary to ensure that the dye is in the same state of aggregation in the two solutions under comparison; pyridine, alcohol or a polyethylene oxide condensate may be added to keep the dye in molecular solution. The solutions to be compared should also be brought to the same pH, e.g. by the addition of acetic acid or ammonia. Vat dyes may be estimated in one of two ways: (a) as the leuco solutions, stabilized by the addition of alcohol or a cellosolve or a polyglycol, and with suitable precautions for avoiding oxidation; (b) by transferring the dye from the aqueous dyebath into boiling *o*-chlorophenol, with the addition of hydrogen peroxide if necessary for oxidizing the dye; the *o*-chlorophenol solution is

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photometric estimation of dyes, detection of impurities, and for some dyestuffs the quantitative estimation of the impurities present. See also Davidson and Godlove, *Am. Dyestuff Reptr.* **39,** 628 (1950); Mellon, Analytical Absorption Spectroscopy, Wiley, New York, 1950.

[86] See Chapter VIII, and Segal, *Compt. rend.* **228,** 204 (1949).

[87] For a description of colorimeters, see F. D. and C. T. Snell, Colorimetric Methods of Analysis, Vol. I, 3rd ed., Van Nostrand, New York, 1948. See also Giles, *J. Soc. Dyers Colourists* **66,** 615 (1950).

[88] For a comparison of these instruments in determining the strengths of dyestuff solutions, see Davies, Giles and Vickerstaff, *J. Soc. Dyers Colourists* **63,** 80 (1947). See also Vickerstaff, The Physical Chemistry of Dyeing, Oliver and Boyd, London, 1950.

cooled, made up to volume and estimated colorimetrically. A third and less satisfactory method is to dissolve a suspension of the oxidized dye in concentrated sulfuric acid and use this solution for colorimetric estimation. Vickerstaff has also submitted the colorimetric estimation of dyes in dyed yarn and fabric to critical examination. The measurement of spectral reflectance, even with the Hardy recording spectrophotometer, is largely empirical; greater accuracy can be obtained by extracting the dye from the fiber with a suitable solvent and then estimating the solution colorimetrically.

Experimental dyeing. Using the fiber or fibers for which the dyestuff is intended and conditions of dyeing which represent large scale practice, the shade and strength of a dyestuff are evaluated practically by experimental dyeings.[57] These are carried out in small beakers or preferably in conical shaped porcelain or stainless steel dye-pots of about 500 cc. capacity. The dye-pots are placed in sets in water-baths which have lids provided with the required perforations, and the baths are filled with a solution of calcium chloride or sodium nitrate so that they may be raised to a temperature of about 125° to enable the dye liquor to be vigorously boiled when necessary. One to ten grams of fiber, as hanks of yarn or pieces of fabric, and twenty times the amount of dyestuff solutions are usually employed. Since very small quantities of dyestuffs and reagents are used in experimental dyeing, they are made up into aqueous solutions of convenient strength and pipetted out as required. A table wringer of the type used in domestic laundrying is an invaluable aid in carrying out experimental dyeings for hydroextracting the material at various stages in the dyeing, developing and soaping processes. Bulk dyeing practice is followed as closely as possible, but there is a considerable gap between the results obtained under experimental and large scale dyeing conditions, and the interpretation of experimental dyeing results for the purpose of applying them to bulk dyeing is only possible in the light of experience.[88a] Experimental padding and jigger dyeing machines are useful for studying the application of dyestuffs to fabrics, but they also yield results which are not strictly comparable with those produced in the full scale machines.

Solubility tests are first carried out, undissolved matter likely to lead to streaky dyeings being indicated by spotting the solution on filter paper. The substantivity of the dyestuff is observed qualitatively by dyeing a full shade (e.g. 2%) under the normal conditions, and determining the dye in the exhaust bath colorimetrically or by dyeing from the exhaust

[88a] Experimental dyeing has been facilitated by the development of the Marney machine in which textile materials of all types can be dyed or wet-treated under reproducible conditions; Marney and ICI, BP 624,054.

bath after measuring its volume and using the proportionate amount of yarn or cloth; the shade from the exhaust is then compared with the original dyeing from a series of solutions of known dyestuff concentration.

Levelling tests. The ability of a dyestuff to give a uniform shade throughout a fibrous material depends on its properties of exhaustion and migration, apart from factors such as suitable pretreatment of the fiber and the use of the correct conditions for dyeing. Exhaustion is the rate of absorption or the percentage of the dyestuff initially present in the dye liquor which is absorbed by the fiber in relation to the time under given conditions of dyeing. The migration of a dye from the heavier dyed to the lighter dyed parts of a fibrous material is a characteristic property which depends on the chemical constitution of the dye. Migrating power is an important factor in level dyeing, since there are practical processes (e.g. the dyeing of cops and cheeses in package dyeing machines) in which heavier dyeing of parts of the material in the early stages cannot be avoided. A dyestuff may yield level dyeings by virtue of two properties; it may be very soluble and dye the fiber readily, the dyestuff from the portions dyed heavily in the initial stages then redissolving in the liquor so that a uniform shade is ultimately obtained; or the dyestuff may go on the fiber at a slow and even rate so that the material appears level dyed continuously and the full shade is gradually built up throughout the material in a uniform manner. The following are among the simple practical tests which indicate the levelling power of a dyestuff:[89] (1) a hank of yarn or a length of narrow fabric is cut in two, and one half of the material is immersed in the dye liquor. After five minutes dyeing under the conditions recommended for the dye, the other half is also introduced and the dyeing continued for a further 15 minutes. The nearer the two halves approach each other in shade the better the levelling power. Alternatively, the material may be left in the dye-bath until the two halves are equal in shade and the time necessary for such equalization noted. In Boulton and Morton's "one-minute strike test" for vat dyes on viscose (see Chapter XXX) a second skein of yarn is introduced one minute after the first and dyeing is continued for 5, 20, 40, 60 and 80 minutes; the differences in shade between the first and second skeins are then graded and recorded as "strike indexes." (2) Small pieces of fabric are successively introduced at short and regular intervals into the dye liquor until it is completely exhausted. The rapidity with which the dyestuff is absorbed and the bath is exhausted is thus readily observed. The compatibility of the dyes in a mixture is indicated by the absence of variation in the tone of the dyeings. (3) The rate of dyeing may be measured quantitatively and plotted as a curve (time against % exhaustion) by any suitable technique in which the concentration of the dye liquor or the quantity of dye on the fiber at definite intervals during one hour (the usual time of dyeing) is determined. The influence of salt (for direct cotton dyes) and other additions to the dyebath on the rate of exhaustion[90] may be similarly determined. The most rapid dyeing dyestuffs often have the best levelling properties, but the latter must be examined directly. (4) A piece of thick tightly woven material is dyed under the usual conditions, and cut in two. The penetration of the dyestuff to the inner portions is then examined visually and microscopically.

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[89] For a graphical representation of the dyeing properties of acid wool dyes in the form of exhaustion and migration curves, see Ris, Stocker and Thommen, *J. Soc. Dyers Colourists* **64,** 297 (1948); see also Leonard *et al.*, *Textile Research J.* **19,** 638 (1949). A Committee of the Society of Dyers and Colourists has recently recommended five tests for determining the optimum conditions under which an acid dye can be applied to wool so as to give an economic degree of exhaustion, as well as a test for measuring the ability of a dye to migrate in the dyebath from one part of the dyed material to another; *J. Soc. Dyers Colourists* **66,** 213 (1950).

The "dyeometer" is an instrument which permits continuous photometric measurement of the strength of the dyebath during the course of dyeing.[91] Rigid control of factors, such as temperature, liquor circulation, and motion of the material being dyed, can be maintained, and the apparatus can be used in the study of any reaction in which a color change within a liquid phase is involved, e.g. reduction rates for vat dyes, rates of chromation, and the stability of dyebaths.

The evaluation of fastness properties has been described in Chapter VI.

Evaluation of pigments. The evaluation of a pigment[69, 92, 93] includes the determination of (a) tinctorial value by mixing with a white pigment (usually zinc oxide) and an oil vehicle, and comparing the tint with a standard; (b) covering or hiding power, which is the ability to hide a surface on which a paint made from the pigment is applied; (c) oil absorption, which is indicated by the quantity of oil required for converting the dry pigment into a stiff paste; (d) tendency to bleed when a paste of the pigment in linseed oil is placed on filter paper; other bleeding tests (using for example water or lacquer as vehicle) may also be carried out; and (e) fastness or durability of the paints, varnishes and lacquers made from the pigment. The physical properties of softness, fineness and texture (particle size and dispersibility by grinding in a vehicle) are carefully examined, since these largely determine the practical utility of a pigment. Moisture and water-soluble matter are estimated, since they represent nontinctorial material and affect the properties of the pigment.

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[90] A Committee of the Society of Dyers and Colourists has surveyed the properties of direct cotton dyes and given details of tests for examining the migration or levelling power and the degree of salt controllability; *J. Soc. Dyers Colourists* **62,** 280 (1946); **64,** 145 (1948).

[91] Royer *et al.*, *Textile Research J.* **16,** 616 (1946); **17,** 447 (1947).

[92] Heaton, Outlines of Paint Technology, 3rd ed., Griffin, London, 1947.

[93] Gardner, Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors, 9th ed., Institute of Paint and Varnish Research, Washington, D.C., 1939.

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